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PUBLICATIONS

Quarterly Progress Report No. 1, July 15, 1951

Quarterly Progress Report No. 2, October 15, 1951

Quarterly Progress Report No. 3, January 15, 1952

Quarterly Progress Report No. 4, April 15, 1952

Quarterly Progress Report No. 5, July 15, 1952

Quarterly Progress Report No. 6, October 15, 1952

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Quarterly Progress Report No. 8, April 15, 1953

Quarterly Progress Report No. 9, July 15, 1953

Technical Report No. 1, Ferroelectricity in the Ilmenite Structure, H. C. Schweinler, October 15, 1951

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SURVEY

In the advanced course which I have been giving this term, I have been treating the energy band theory. I had hoped to get further; but it has taken the entire term to cover the material. This includes just Chapter 1 of the proposed report on "Electronic Structure of Solids". Under the circumstances, it has seemed best to include just this chapter on energy bands in the Technical Report No. 4, and this report, including also a bibliography of papers on energy bands, is being prepared for the printer, and should be sent out not long after this Progress Report. I had hoped also to treat the use of Wannier functions in discussing lattice imperfections and excitons, and various applications of configuration interaction in solids, including ferromagnetism. Since this material was not covered, I shall propose to take it up in a continuation of the same course in the fall, and shall write the proposed additional chapters of the report on "Electronic Structure of Solids" at that time, bringing them out as a further Technical Report No. 5 at a later date.

This course on the theory of energy bands has furnished an occasion for examining the relative merits of the various methods in current use for studying energy bands. The conclusion to which we have been led is that the orthogonalized plane wave method, perhaps modified to Herman's "augmented orthogonalized plane wave method", is the most promising method at present for accurate numerical work. Parmenter's attempt to apply the tight binding approximation accurately to chromium has shown the almost impossible complexity to which that method leads when we try to apply it accurately; the orthogonalized plane wave method seems clearly simpler. Parmenter accordingly is looking into ways of applying this method to chromium.

The great drawback of the orthogonalized plane wave method is that it is not readily adaptable to values of the propagation constant other than a few special points in the unit cell, such as the center of the Brillouin zone and a few other points. The reason is that at these symmetry points, a number of plane waves must have identical coefficients, so that the number of distinct coefficients is relatively small, even for a sum of a large number of plane waves, and we do not face a very difficult secular equation. A method of interpolation between these symmetry points is highly desirable. With this in mind, it occurred to me that the tight binding approximation might furnish a good interpolation method, if the various integrals which occur in it were regarded as disposable parameters, rather than quantities to be calculated from wave functions and potentials. Dr. Koster and I have been examining this possibility, and it seems very encouraging. In particular, we have carried through a study of the diamond lattice, fitting the points determined by Herman by the orthogonalized plane wave method, and

our solution, which describes both the valence and conduction band, seems very likely to be rather close to the truth. We find that we can get this fit by using only nearest and second nearest neighbor interactions, and including no three-center or overlap integrals; there are enough remaining integrals to use as disposable parameters. Fortunately, the integrals derived by fitting Herman's values have entirely reasonable values, having the correct signs and relative magnitudes, so that this procedure seems entirely reasonable. We are carrying this method further, considering somewhat more complicated crystals. This work is report partly in the present Progress Report, partly in Technical Report No. 4. We are indebted to Dr. F. Herman, of R.C.A., for valuable help in this problem; he has also been independently considering the tight binding approximation for interpolation purposes.

The work on a two-electron model of ferromagnetism, on which Drs. Statz and Koster and I have reported in the two preceding Progress Reports, has been written up for submission to the Physical Review. Drs. Statz and Koster give in this Progress Report a two-dimensional model, coming a little closer to the truth than the one-dimensional model which I presented in the preceding Progress Report, and which is partly incorporated in the Physical Review paper. As for future work on this theory, we feel that we want to get closer to the actual structure of a ferromagnetic metal, such as nickel, and this demands knowing something about the Wannier functions and energy bands. We are delaying work in this direction, on account of the feeling that the tight binding interpolation method, which I have just been describing, may well be adapted to such energy bands, and to the Wannier functions to be formed from them. Dr. Kikuchi, meanwhile, is looking at a very simplified two-atom model, in the hope that he will find a ferromagnetic ground state which may well have analogies to the ground state in more complicated systems.

Dr. Pratt continues to work on the problem of antiferromagnetism, which is one of the most intricate problems which we face. His two communications, and one of Dr. Koster on an extension of Hund's rule, all have a bearing on this problem, whose status is something of the following sort. We have examined a number of models; and the difficulty which arises is that there is a great tendency for a ferromagnetic, rather than an antiferromagnetic, state to lie lower. This is probably a result of the method of approximation, but it illustrates the extreme sensitivity of the problem, and the need of examining it very carefully before we really understand the validity of the various approximations. In particular, Koster shows that Hund's rule, stating that the ferromagnetic state will lie lower, holds for any case, molecular as well as atomic, in which our configuration interaction problem is an ordinary spin degeneracy problem between orthogonal orbitals. Probably as a result of this, Pratt finds that the model which he has set up of a triatomic molecule $(MnOMn)^{++}$ has a ferromagnetic state as its ground state, though we had hoped that we should find an antiferromagnetic ground

state, and so an explanation of superexchange. We are not satisfied, however, that this result is correct, for very likely a much more extensive configuration interaction is needed to lead to a possible antiferromagnetic ground state.

The writer suspects that the actual situation is the following. He has pointed out on several occasions that the effective potential energy in which an electron of + spin moves may be different from that for an electron of - spin on account of exchange effects, the electron of + spin has a lower potential energy when it is in a distribution of charge of other + electrons, and a higher potential energy when surrounded by electrons of - spin. If we then have an antiferromagnetic configuration of $(MnOMn)^{++}$, the spins on one of the Mn ions (which will certainly all be parallel to each other in the ground state, by Hund's rule for the Mn ion) will point in one direction, say +, while those on the other Mn ion will point in the other direction, say -. An electron of + spin, then, will find a lower potential well in one Mn ion than in the other. This will hold for the electrons of oxygen, as well as for those of the manganese. Thus the electrons of + spin in the oxygen will find themselves effectively in a strong field, pulling them toward the manganese ion with + spin, while the electrons of - spin in the oxygen will find themselves in an equal field in the opposite direction. These electrons will be polarized by these fields, just as if the fields were ordinary electrostatic fields, and this will reduce the energy of the molecule. A corresponding polarization will not occur in the ferromagnetic case, for then the electrons of each spin, in the oxygen, will find themselves effectively in zero field. The writer suspects that it is the lowering energy on account of this polarization which stabilizes the antiferromagnetic state.

This picture of the role of the oxygen atoms supplements the remarks made by the writer several years ago, regarding the alternating potential in which an electron finds itself, in an antiferromagnetic crystal. It was pointed out that this alternating potential would split the energy bands apart, the unit cell in the crystal being twice as great as ordinarily considered, and that in some cases we could well have the lower band filled, the upper one empty, thus explaining the non-conducting properties of certain antiferromagnetic crystals which otherwise would be thought to be conductors. But this argument by itself does not show why the antiferromagnetic crystal has a lower energy than the ferromagnetic arrangement. Dr. Pratt reported some time ago on having looked into a one-dimensional model of such a system, and he found the ferromagnetic state to have the lower energy. It now seems likely that the presence of the oxygen is required to stabilize the antiferromagnetic state, in the way described above, though the splitting of the energy bands would take place just as described earlier by the writer.

The problem is then simply to find the correct way to describe this polariza tion of the oxygens. This could be done by a configuration interaction with excited states of the oxygen atom, but this is a notoriously poor way to describe polarization,

from the point of view of convergence. It is much better to modify the wave function, in the way which Mr. Allen is investigating, using a single determinant made of orbitals which are distorted as they would be in the presence of a field. In our case, the oxygen orbitals corresponding to electrons of one spin would be distorted in one direction, those corresponding to the other spin in the other direction, so that they would no longer be identical to each other. All this is easier to describe in simple language, than it is to carry out in detail. For one thing, we are dealing with a singlet state of the molecule, and we cannot say in any proper way that the spin of one manganese ion is pointed in one direction, that of the other ion in the other direction; the true wave function is a combination of wave functions of the two manganese ions, with a variety of orientations. The process of building up the wave function out of determinants is extremely complicated, on account of the many electrons involved; it is this part of the problem that Dr. Pratt is handling by his operator method. Finally, if the suspicions regarding polarization are correct, it may be necessary to use non-orthogonal orbitals, and the technique for doing this properly, without neglect of the overlap integrals, which may be the essential feature in the problem, is very complicated. The problems which Dr. Pratt is facing are not so much problems of visualizing the qualitative nature of the solution, as those of formulating the solution in mathematical language in which we are sure that we are not throwing away the essential terms by mistake. A simplified model which he has been considering, since treating the cases described in this Progress Report, gives hope for thinking that we are on the right track in our thinking about the polarization of the oxygen.

The various investigations into molecular structure are progressing. An important result of our consideration of configuration interaction has been the conviction that there are very few cases simple enough to handle by a complete configuration interaction. If we use only a partial configuration interaction, it then is very important to have good molecular orbitals to start with. There are very few cases in the literature in which really good calculations of molecular orbitals, by a self-consistent method, have been carried out. Accordingly, Dr. Meckler has considered the possibility of mechanizing the problem of determining self-consistent LCAO molecular orbitals, and has found a way to do it on the Whirlwind Digital Computer, which he described in the present Progress Report. If this procedure can be actually put into operation, it might mean an important advance in the problem of finding molecular orbitals.

The mechanization of the calculation of the integrals needed for the water problem, by Koster and Schweinler, is proceeding. This calculation, Meckler's on ethane, Kaplan's on ammonia, Barrett's on fluorine, and Corbato's on HF, all tie in together in the calculations of integrals, and general procedure, and are all progressing, though slowly. Unfortunately the calculation of HF by Mr. Merrifield, reported

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on in preceding Progress Reports, had to be discontinued at a point where it had not yielded useful numerical results; a continuation of this program is being studied by Mr. Corbato. Various other somewhat disconnected pieces of work are under way, as will be evident from the Progress Report.

There has been one change in the personnel of the group since the preceding Progress Report: Dr. Statz has left the group to join the staff of the Raytheon Manufacturing Company. Fortunately, he will still be in the neighborhood, so that he will be able to join in the general scientific activities of the group. Various other changes in personnel are in prospect for the summer and the next academic year.

J. C. Slater

1. A SIMPLIFIED TIGHT BINDING METHOD FOR ENERGY BANDS

Among all the methods which have been used for studying energy bands, the tight binding approximation, or Bloch method, has one outstanding advantage: it gives simple analytical formulas for the energy as a function of the propagation constant. It has compensating disadvantages, however: to carry it through really rigorously, taking into account all three-center integrals, overlap integrals, and other complicating features, is practically impossible, as Dr. Parmenter's attempt to apply it to the energy bands of chromium has shown. It has occurred to the writers, however, that the method could be extremely useful as an interpolation method, for getting the energy as a function of propagation constant in a case where accurate values of the energy were known at certain symmetry points in the reciprocal space. This method has been written up in fair detail in the Technical Report No. 4, which will appear shortly, and for that reason only a sketch of the work so far done will be given in this Progress Report.

Of all methods which have been used up to the present for energy bands, the orthogonalized plane wave method seems to the writers to be probably the one best adapted to getting accurate values of the energies. The study which Herman[1] has made of diamond and germanium gives one the feeling that the results are very reliable; particularly the indication that the method is converging rapidly as more and more terms are added to the series is very encouraging. On the other hand, the orthogonalized plane wave method is not well adapted for calculations except at particular symmetry points in the reciprocal space. The reason for this is very simple: at a symmetry point, many plane waves must have identical coefficients, so that the number of independent coefficients is far less than the number of plane waves which are being superposed to get an approximate solution of Schrödinger's equation. Thus, for instance, the greatest number of independent coefficients which Herman used in his study of diamond was 16, so that he had to solve a 16-by-16 secular equation; but the wave function in this case was made of 146 plane waves. For a propagation constant not having special symmetry, we should still need 146 plane waves to get comparable accuracy, but now there would be no special relations between their coefficients, and a 146-by-146 secular equation would be required, which of course would be beyond our present capabilities.

We are then faced with a situation where we have very good energy values for certain values of the propagation constant, without an equally good way to interpolate between them. For instance, in the cases of diamond and germanium mentioned above, we have values for the center of the central Brillouin zone, and for the boundaries of the zone along the 100 and 111 directions. It has now occurred to Herman,[2] as well as to the writers, that it might be possible to use a very much simplified tight binding method, but to choose the parameters entering into this method, not by direct calculation from atomic wave functions and potentials, but by regarding them as arbitrary parameters, to be chosen so as to fit the values which were accurately known. We

might then hope that the solutions of the tight binding problem would give acceptable interpolation values for the energy. Since we are using the method only for interpolation, we can afford to make simplifications which would be entirely inadmissible if we were using it for an original calculation: we can disregard interaction integrals between distant neighbors, we can neglect all integrals except two-center integrals, and all overlap integrals. We still keep enough terms, however, to have enough disposable constants to fit the values which we assume known; and of course we must keep such terms that we have a good hope that the calculation will agree with the correct one to an adequate accuracy.

To illustrate the method, we have made a fairly complete study of the diamond crystal, fitting our constants to Herman's values. We start with the two interpenetrating face-centered cubic lattices which form the diamond crystal. We form Bloch waves from s, p_x, p_y, p_z orbitals on one of the lattices, and similar waves from the same orbitals on the other lattice. We have, then, eight Bloch waves, and we set up a secular equation between these eight function for a given value of the propagation constant. In this secular equation, we disregard all overlap integrals between atomic orbitals on different atoms. The matrix components of energy involve integrals of the form $\int \phi_a^*(\vec{r}) H \phi_b(\vec{r} - \vec{R}) dv$, where ϕ_a and ϕ_b are two atomic orbitals, (for instance, an s and a p_x orbital), $\vec{R}$ is one of the displacement vectors from one atom to another, and H is the one-electron Hamiltonian operator of the periodic potential problem. It is well known that this integral can be reduced to a sum of integrals of the form $\int \phi_a^*(\vec{r})$ $V(\vec{r} - \vec{R}') \phi_b(\vec{r} - \vec{R}) dv$, where the potential H is expressed as a sum of terms $V(\vec{r} - \vec{R}')$, spherically symmetrical potentials about the atoms located at positions $\vec{R}'$, to an approximation which is sufficient for the present purposes. The integral above is a three-center integral, provided $\vec{R}$ and $\vec{R}'$ are different from each other and from zero. We disregard all such terms, and consider only the two-center integrals where $\vec{R}'$ equals $\vec{R}$ or zero. Then our integrals are like those found in a diatomic molecule. We can simplify them by expanding the ϕ's in terms of functions quantized with respect to the axis $\vec{R}$ of the pair of atoms. Thus if we are dealing with p orbitals, we have $p\sigma$ and $p\pi$ components with respect to the axis. We have non-vanishing integrals only if both ϕ_a and ϕ_b have the same component of angular momentum about the axis; that is, if both are σ, or π, or δ functions. We have integrals, then, of types which can be symbolized by the azimuthal quantum numbers of both orbitals (denoted by s or p in this case), and by the component of angular momentum about the axis (σ or π in this case). Such integrals can be denoted in an obvious way as (ssσ), (spσ), (ppσ), (ppπ), and depend of course on whether we are dealing with nearest neighbors, next nearest, and so on; this can be denoted by subscripts 1, 2, etc. It is these various integrals which we regard as the disposable parameters of the problem.

We have set up formulas for all matrix components of energy, diagonal and

non-diagonal, between the various Bloch functions in terms of these integrals. We then have, in our case of diamond, an eight-by-eight secular equation between the Bloch functions. This equation can be easily solved analytically at the required symmetry points, and we can get solutions involving nothing worse than a biquadratic equation along the 100 and 111 directions. We can now try to fit all of Herman's values at the symmetry points. We find that, using nearest and second nearest neighbors, we do not have quite enough disposable constants to fit all of these values. However, we can adjust the constants to fit them all with only small errors. In other words, there are relations between Herman's values which almost, though not quite, make tnem compatible with a solution involving only second nearest neighbors. When we do this, the resulting constants are interesting, in that the integrals for second nearest neighbors come out much smaller than those for nearest neighbors, suggesting that we really have a convergent process. The integrals for nearest neighbors have the signs and general magnitudes which we should expect; for instance, $(pp\pi)$, the interaction between $p\pi$ orbitals on the two atoms, comes out considerably smaller numerically than $(pp\sigma)$, the interaction of $p\sigma$'s on the two, as we should expect since the $p\sigma$'s overlap more.

When we use these constants, we then can get solutions for other points of the momentum space; we have carried out solutions along the 100 and 111 directions (except that we have so far not solved for the states which require a biquadratic equation). The energies resemble the interpolations which have been used by Herman in his papers, but differ in some respects; these solutions are given in Technical Report No. 4. The qualitative behavior of the solutions is as given by Herman. Also the solutions in the neighborhood of the degeneracies, as in the neighborhood of the three-fold degenerate states at $\vec{k} = 0$, have the behavior which we must expect from symmetry, and which has been described by Shockley.[3]

The method which we have described for diamond will be recognized as essentially equivalent to that proposed by Morita.[4] His formulas for the matrix components of energy are essentially like ours, except that he does not express his integrals in terms of our quantities such as $(ss\sigma)$, etc. He finds his integrals from atomic orbitals and potentials. We have worked backward from Morita's published values of his integrals, to see the values which he must have found for the various integrals which we have determined by fitting Herman's values. In doing so, we have observed what appears to have been an error of some sort in Morita's integrals. Specifically, he finds a numerically greater value for his integral which we denote by $(pp\pi)$ than for $(pp\sigma)$, contrary to our findings, and contrary to what one would expect from straightforward calculation. This apparent error in Morita's calculation seems to explain another feature of his results. He found that the lowest energy in the conduction band, for $\vec{k} = 0$, came from an s-like rather than from a p-like state, contrary to Herman's result. We,

however, have been able to find values of the integrals which not only put the levels in the same order as found by Herman, but agree quite well quantitatively with Herman's results. We feel, therefore, that the doubts about the tight binding approximaticn expressed by Herman in the reference quoted are not justified.

A different sort of tight binding approach has been carried out by Hall,[5] though he does not like to admit that his method is really a tight binding calculation. He starts with what he calls equivalent orbitals. We can describe these in the following fashion. We start with tetrahedral directed orbitals on each of the atoms of the crystal, directed toward the neighboring atom. We then make a symmetric combination of the two directed orbitals at the two ends of each bond, and call this symmetric combination an equivalent orbital. We have four such equivalent orbitals per unit cell of the crystal, so that we can make four Bloch combinations of them. We then can set up matrix components of the energy between these four Bloch functions, and can solve a four-by-four secular equation between them. This secular equation will have four roots, which may be expected to describe the four levels in the valence band of diamond. It is this secular equation which Hall has considered.

The results which he has found are not in good agreement with those of Herman; in particular, Hall, like Kimball and Hund and Mrowka[6] with the cellular approximation, finds a doubly degenerate state whose energy is independent of the propagation vector, whereas Herman finds that the energy of this state is a function of $\vec{k}$, and it is split in certain directions; our tight binding calculation agrees entirely with Herman in these respects. One way of describing this shortcoming of Hall's treatment is that he takes into account only interactions of nearest neighbors; if he considered more distant neighbors, he could get a suitable behavior. In fact, Herman[7] has found it possible to get a good fit with his values by making up equivalent orbitals like Hall's, and using sufficiently distant neighbor interactions. The interactions must be assumed significant out to considerably more than the second nearest neighbors, however, which are the only ones which we need use in our method of formulation, in which we get the conduction band as well as the valence band from and eight-by-eight secular equation.

One can easily convert Hall's calculation into one equivalent to ours, and it is instructive to see how this is to be done. Just as Hall has set up four Bloch functions from the symmetrical equivalent orbitals, we could make antisymmetric equivalent orbitals, and make four Bloch functions from them. The four-by-four secular equation resulting from these would give a description of the conduction band. But we should find that there were non-diagonal matrix components of energy between the four Bloch functions formed from the symmetric orbitals, and the four formed from the antisymmetric orbitals. These non-diagonal matrix components vanish for $\vec{k} = 0$, but become larger as we go out in the Brillouin zone. If we now consider all eight of these Bloch functions, and the eight-by-eight secular equation between them, we can show that it is

equivalent to the problem as we have set it up. We can get satisfactory results in this case by considering only nearest and second nearest neighbors, while to get satisfactory results from Hall's procedure we need terms coming from more distant neighbors. The easiest way to remove the zero-width bands, then, is to consider interaction between the valence and conduction band. The point is that except at $\vec{k} = 0$, the wave functio.·s of the valence band are not constructed entirely from the symmetric combinations of orbitals on the two lattices, and the conduction band entirely from the antisymmetric combination; closer examination of the wave functions shows that the phase difference between the waves on these two lattices changes from zero or 180° at $\vec{k} = 0$ (for the symmetric and antisymmetric solutions) to 90° at the edges of the band, a situation which can be described by Hall's method only with difficulty.

We are examining the tight binding approximation further, and hope to come back to the relation between it and the Wannier functions for overlapping bands.

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3. W. Shockley, Phys. Rev. 78, 173 (1950).

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J. C. Slater and G. F. Koster

2. ENERGY BANDS IN CHROMIUM

The original plan of calculating electronic energy bands in chromium, reported in previous Progress Reports, involved expanding the valence-electronic wave functions as arbitrary linear combinations of orthogonalized plane waves plus 3d Bloch functions. Each 3d Bloch function was to be a so-called Bloch sum of 3d atomic orbitals associated with the isolated chromium atom. In calculating matrix elements of the crystal potential between two 3d Bloch waves, there arise terms involving three-center atomic integrals (the one-electron integral of a product of an atomic potential centered on one lattice site and two 3d atomic wave functions centered on two different lattice sites). Because of the difficulty in accurately calculating three-center integrals, the above scheme is not feasible as it stands.

Let us suppose, however, that the 3d atomic orbitals are modified in such a way that they vanish at distances greater than one-half the nearest neighbor distance in chromium. All three-center integrals will now vanish, and there will be no difficulty in calculating matrix elements of the crystal potential. Such a method should be generally useful among the transition elements. It has been suggested by Herman[1] that the same method (which he calls the augmented orthogonalized plane wave method) should be more rapidly convergent than the orthogonalized plane wave method alone when dealing with valence crystals (such as diamond) or semiconductors (such as germanium). With regard to transition elements, the motivation of the AOPW method is to represent by orthogonalized plane waves that portion of the crystal wave function resulting from both 4s atomic orbitals and the overlapping portions of 3d atomic orbitals and to represent by Bloch waves that portion of the crystal wave function resulting from the non-overlapping portions of the 3d atomic orbitals.

The method to be used in modifying the 3d atomic orbitals is more or less arbitrary, of course, but the following method, which has been used on chromium, seems physically reasonable and probably can be used whenever the AOPW method is applicable. Let us construct an atomic orbital by numerically integrating Schrödinger's equation with a Hamiltonian containing the crystal potential, the numerical integration starting at any nucleus of the crystal. Since we desire an orbital of definite angular momentum ($l = 2$), we must use the spherical average of the crystal potential in Schrödinger's equation. This spherical average can be approximated by the isolated-atom potential $V(r)$ for $r < R$ and by the constant $V(R)$ for $r > R$. The radius R is chosen such that $V(R) = \langle V(r) \rangle$, where $\langle V(r) \rangle$ is the average value of $V(r)$, averaged over the unit cell of the crystal. It seems reasonable to take the orbital equal to the isolated-atom 3d orbital for $r < R$; i.e., we use the energy of the isolated-atom 3d orbital as the energy used in numerically integrating Schrödinger's equation. For $r > R$, the numerically integrated orbital will deviate sharply from the isolated-atom wave function since the spherical average of the crystal potential is lower than the isolated-atom potential. This will result in a radial node in the orbital at some value of r which is approximately

equal to one-half of the nearest neighbor distance in the crystal. (For chromium $R =$ 1.55 atomic units, the radial node in the numerically integrated orbital occurs at 2.80 atomic units, while one-half of the nearest neighbor distance is 2.36 atomic units.) By cutting off the numerically integrated orbital beyond the radial node, we have formed a modified 3d orbital suitable for our purposes.

Reference

1. F. Herman, Ph.D Thesis, Department of Physics, Columbia University, January, 1953, p. 40.

R. H. Parmenter

3. A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM

In the previous two Progress Reports, J. C. Slater,[1] H. Statz,[2] and G. F. Koster[3] have discussed a two-electron example of ferromagnetism. In this Progress Report we apply the same methods to a simple two-dimensional case. This case further confirms the necessity of degenerate bands for ferromagnetism and also illustrates some of the techniques which would be useful in a more detailed discussion of ferromagnetism.

A two-electron function in a crystal may be expanded in terms of products of Wannier functions associated with the various energy bands of the crystal.

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{i,j,m,n} U_{ij}(\vec{R}_n, \vec{R}_m)\, a_i(\vec{r}_1 - \vec{R}_n)\, a_j(\vec{r}_2 - \vec{R}_m) \qquad (3.1)$$

Here i refers to the band from which the Wannier function a_i arises, $\vec{r}_1$ and $\vec{r}_2$ are the coordinates of the two electrons, and $\vec{R}_n$ is one of the primitive translations of the crystal. We know, however, that the symmetry properties of a wave function depend only on the invariances of the Hamiltonian and not on the number of electrons the wave function describes. We expect therefore that all the discussion of the irreducible representations of the space groups by Seitz[4] and others[5] will be applicable here. In particular, we are able to define a $\vec{K}$ vector which expresses the fact that our two-electron wave function goes into $e^{i\vec{K} \cdot \vec{R}_p}$ times itself under translation through $\vec{R}_p$. This allows us to write our $U_{ij}(\vec{R}_n, \vec{R}_m)$ in a simpler form

$$U_{ij}(\vec{R}_n, \vec{R}_m) = e^{i\vec{K} \cdot \frac{\vec{R}_n + \vec{R}_m}{2}}\, F(\vec{R}_n - \vec{R}_m) \qquad (3.2)$$

More can be said since we know that our Wannier functions may have certain symmetry properties. Let us see how this influences our F's. We restrict our attention to $\vec{K} = 0$. (The following arguments could be easily carried out for other $\vec{K}$ values.) We must first see what effect some operation a of our point group has on the wave function since we know that the wave functions for $\vec{K} = 0$ must form irreducible representations of the point group of the crystal. It can easily be seen that

$$a\psi(\vec{r}_1, \vec{r}_2) = \sum_{i,j,p,m} F(a^{-1}\vec{R}_m)\, a a_i(\vec{r}_1 - \vec{R}_p)\, a a_j(\vec{r}_2 - \vec{R}_p + \vec{R}_m) \qquad (3.3)$$

Here $a a_i(\vec{r})$ is the Wannier function which results from applying the operation a to $a_i(\vec{r})$. $a^{-1}\vec{R}_m$ is the primitive translation arrived at by applying a^{-1} to $\vec{R}_m$. Since we know the transformation properties of our Wannier functions from Eq. (3.3) we are able to get relations between our $F(\vec{R}_m)$'s. This is most easily seen by a simple example.

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

Assume that our two-electron wave function is derived from the Wannier functions of a single non-degenerate band for which $\alpha a(\vec{r}) = a(\vec{r})$ is true for all α. Let us look for the two-electron wave function that forms a completely symmetric representation of our point group ($\alpha \psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1, \vec{r}_2)$; for all α). By applying these relations to Eq. (3.3) we get

$$\sum_{p, m} F(\vec{R}_m) a(\vec{r}_1 - \vec{R}_p) a(\vec{r}_2 - \vec{R}_p + \vec{R}_m) = \sum_{p, m} F(\alpha^{-1} \vec{R}_m) a(\vec{r}_1 - \vec{R}_p) a(\vec{r}_2 - \vec{R}_p + \vec{R}_m)$$

(3.4)

$$\text{therefore } F(\vec{R}_m) = F(\alpha^{-1} \vec{R}_m)$$

The additional symmetry property of our two-electron wave function concerns its value of total spin. This is determined by the relation

$$F(-\vec{R}_m) = \pm F(\vec{R}_m)$$

(3.5)

The $-$ sign refers to the triplet and the $+$ sign refers to the singlet.

Let us now apply the preceding discussion to a two-dimensional square lattice. We wish to determine our F's by minimizing the expectation value of a two-electron Hamiltonian

$$H = H_1 + H_2 + g_{12}$$

(3.6)

where H_1 and H_2 are the one-electron Hamiltonians of our two electrons in a periodic potential and g_{12} is the Coulomb repulsion between two electrons or two holes. We study first a non-degenerate band for which $\alpha a(\vec{r}) = a(\vec{r})$ for all α of the point group. This gives rise to the secular equation (Ref. 1, Eq. (1.6))

$$\sum_p 2 \mathscr{E}(\vec{R}_p) F(\vec{R}_n + \vec{R}_p) + \delta(\vec{R}_n, 0) V_o = E F(\vec{R}_n)$$

(3.7)

Here

$$\mathscr{E}(\vec{R}_p) = \int a(\vec{r}_1) H_1 a(\vec{r}_1 - \vec{R}_p)$$

$$V_o = 2 \int \frac{a(\vec{r}_1) a(\vec{r}_1) a(\vec{r}_2) a(\vec{r}_2)}{r_{12}} = (aa|aa)$$
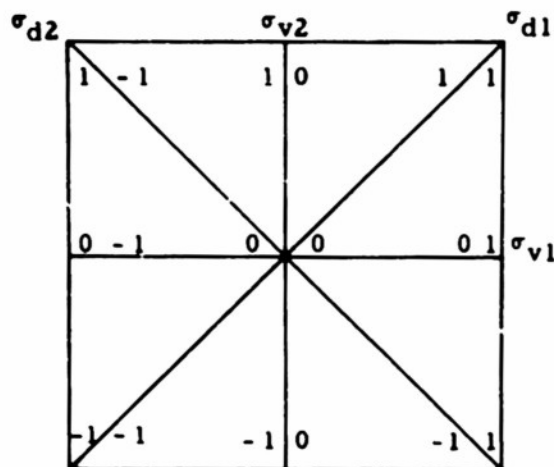
Fig. 3-1

Square lattice in R_1 - R_2 space. The figure gives the notation
for the g lattice points and the various "planes" of reflection.

In this secular equation the assumption has been made that two electrons interact only
when they are at the same lattice site. We also assume $\mathscr{E}(\vec{R}_p)$ = 0 except for nearest
neighbor interactions. For boundary conditions in relative coordinate space we make
the assumption that $F(\vec{R}_n)$ vanishes on the sides of a square that contains nine lattice
sites. Fig. 3-1 contains a diagram of this region of relative coordinate space as well
as labels for the various lattice points under consideration. Table 3-1 gives the vari-
ous irreducible representations of group C_{4v} (the point group of a square lattice). The
σ's are reflections through the "planes" indicated in Fig. 3-1. C_4 is a clockwise rota-
tion through 90° and C_2 = $C_4^{\,2}$.

Table 3-1

Character table for the group of the square lattice C_{4v}

Operation Representation	E	C_2	$C_4, C_4^{\,3}$	σ_{v1}, σ_v	σ_{d1}, σ_{d2}
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	1	-1	1	-1
B_2	1	1	-1	-1	1
E	2	-2	0	0	0

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

We will now discuss in detail one of the symmetries of two-electron wave functions for $\vec{K} = 0$ under the above assumptions. Let us look at those wave functions with A_1 symmetry. Using the relation (3.4) we see at once that

$$F(1, 1) = F(1, -1) = F(-1, -1) = F(-1, 1) = \frac{\gamma}{2}$$

$$F(1, 0) = F(0, 1) = F(-1, 0) = F(0, -1) = \frac{\beta}{2} \tag{3.8}$$

$$F(0, 0) = \alpha$$

Substituting these relations into secular equation (3.7) we find

$$\alpha(V_0 - E) + \frac{\beta}{2}(8\mathcal{E}) + \frac{\gamma}{2}(0) = 0$$

$$\alpha(2\mathcal{E}) + \frac{\beta}{2}(-E) + \frac{\gamma}{2}(4\mathcal{E}) = 0 \tag{3.9}$$

$$\alpha(0) + \frac{\beta}{2}(4\mathcal{E}) + \frac{\gamma}{2}(-E) = 0$$

therefore

$$E^3 - V_0 E^2 - 32\mathcal{E}^2 E + 16\mathcal{E}^2 V_0 = 0 \tag{3.10}$$

Here $\mathcal{E}$ is the nearest neighbor interaction (that is, the matrix element of the one-electron Hamiltonian between a Wannier function at $(0, 0)$ and one at $(0, 1)$). The equation (3.10) can be solved for small $\mathcal{E}$ giving the result

$$E = V_0 + \frac{16\mathcal{E}^2}{V_0}$$

$$E = \pm 4\mathcal{E} - \frac{8\mathcal{E}^2}{V_0} \tag{3.11}$$

These states are clearly singlet states since $F(\vec{R}_n) = + F(-\vec{R}_n)$. A similar discussion can be carried out for the other symmetries. First we write down the relations between the F's which result from the irreducible representation which we desire and the symmetry properties of the Wannier functions. We then use these relations to simplify the secular equation (3.7) and finally we find approximate eigenvalues of the secular equation if these equations are above the second order.

For A_2 symmetry we find that all the F's must vanish and therefore we cannot find a state of this symmetry.

For B_1 symmetry we find

$$F(1, 1) = F(-1, 1) = F(1, -1) = F(-1, -1) = 0$$

$$F(0, 1) = F(0, 1) = F(1, 0) = -F(-1, 0) = \frac{a}{2} \tag{3.12}$$

$$F(0, 0) = 0$$

which leads to the secular equation

$$\frac{a}{2}(-E) = 0; \quad E = 0 \tag{3.13}$$

This is a singlet.

For B_2 symmetry we find

$$F(1, 1) = F(-1, -1) = -F(-1, 1) = -F(1, -1) = \frac{a}{2}$$

$$F(0, 1) = F(1, 0) = F(-1, 0) = F(0, -1) = 0 \tag{3.14}$$

$$F(0, 0) = 0$$

This gives rise to the secular equation

$$\frac{a}{2}(-E) = 0; \quad E = 0 \tag{3.15}$$

once again this is a singlet.

For E symmetry we have a doubly degenerate wave function. In this case we set up two wave functions

$$\psi_x = \sum F^x(\vec{R}_m) a(\vec{r}_1 - \vec{R}_p) a(\vec{r}_2 - \vec{R}_p + \vec{R}_m)$$

$$\psi_y = \sum F^y(\vec{R}_m) a(\vec{r}_1 - \vec{R}_p) a(\vec{r}_2 - \vec{R}_p + \vec{R}_m) \tag{3.16}$$

Here ψ_x and ψ_y transform as x and y do under the operations of the group of the square. Once again this gives us relations between the F's

$$F^x(1, 1) = F^x(-1, 1) = -F^x(-1, -1) = -F^x(1, -1) = \frac{\beta}{2}$$

$$F^y(1, 1) = -F^y(-1, 1) = -F^y(-1, -1) = F^y(1, -1) = \frac{\beta}{2} \tag{3.17}$$

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

$$F^x(0,1) = -F^x(0,-1) = F^y(1,0) = -F^y(-1,0) = \frac{a}{\sqrt{2}}$$

$$F^x(1,0) = F^x(-1,0) = F^y(0,1) = F^y(0,-1) = 0 \qquad \text{(3.17) con'd.}$$

$$F^x(0,0) = F^y(0,0) = 0$$

The secular equation for the x-like functions is

$$\frac{a}{\sqrt{2}}(-E) + \frac{\beta}{2}(4\delta) = 0$$

$$\text{(3.18)}$$

$$\frac{a}{\sqrt{2}}(2\delta) + \frac{\beta}{2}(-E) = 0$$

with roots

$$E = \pm 2\sqrt{2}\,\delta$$

Thus we get two doubly degenerate eigenvalues (a total of four wave functions). These states are all triplets ($F(\vec{R}_n) = -F(-\vec{R}_n)$). Fig. 3-2 contains a graph of energy as a
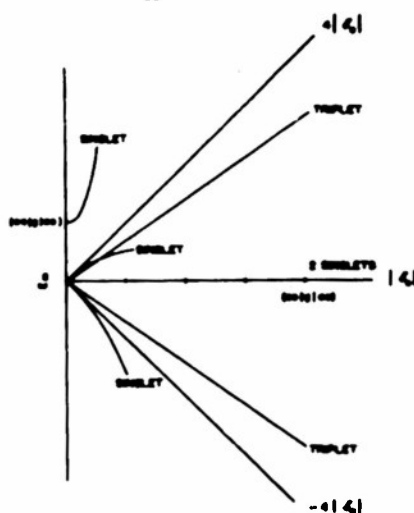
Fig. 3-2

Energy as a function of nearest neighbor inter-
action δ for the case of non-degenerate bands.

function of δ for the two-electron states arising from a non-degenerate band. We notice that the singlet state of A_1 symmetry is the lowest state. The fact that the singlet lies lower than the triplet we interpret as an absence of ferromagnetism.

We now consider the case of two degenerate bands which we describe in terms of Wannier functions with x- and y-like symmetry.[6] We will call them $a(\vec{r})$ and $b(\vec{r})$ and their symmetry properties are given in Table 3-2.

Table 3-2

Symmetry properties of Wannier functions a and b

Operation	b	a
E	b	a
C_4	- a	b
C_2	- b	- a
$C_4{}^3$	a	- b
σ_{d1}	a	b
σ_{d2}	- a	- b
σ_{v1}	b	- a
σ_{v2}	- b	a

We write our two-electron function as

$$\psi(\vec{r}_1, \vec{r}_2) = \sum F_{aa}(\vec{R}_m)\, a(\vec{r}_1 - \vec{R}_p)\, a(\vec{r}_2 - \vec{R}_p + \vec{R}_m)$$

$$+ \sum F_{bb}(\vec{R}_m)\, b(\vec{r}_1 - \vec{R}_p)\, b(\vec{r}_2 - \vec{R}_p + \vec{R}_m)$$

$$+ \sum F_{ab}(\vec{R}_m)\, a(\vec{r}_1 - \vec{R}_p)\, b(\vec{r}_2 - \vec{R}_p + \vec{R}_m)$$

$$+ \sum F_{ba}(\vec{R}_m)\, b(\vec{r}_1 - \vec{R}_p)\, a(\vec{r}_2 - \vec{R}_p + \vec{R}_m)$$

(3. 19)

If we assume that there is only interaction between electrons when they are at the same lattice site, these functions give rise to the secular equations[1]

$$\sum_p 2\mathscr{E}_a(\vec{R}_p)\, F_{aa}(\vec{R}_n + \vec{R}_p) + \delta(\vec{R}_n, 0)\left[F_{aa}(0)(aa|aa) + F_{bb}(0)(ab|ab)\right] = E F_{aa}(\vec{R}_n)$$

$$\sum_p 2\mathscr{E}_b(\vec{R}_p)\, F_{bb}(\vec{R}_n + \vec{R}_p) + \delta(\vec{R}_n, 0)\left[F_{bb}(0)(bb|bb) + F_{aa}(0)(ab|ab)\right] = E F_{bb}(\vec{R}_n)$$

$$\sum_p \left[\mathscr{E}_a(\vec{R}_p) + \mathscr{E}_b(\vec{R}_p)\right] F_{ab}(\vec{R}_n + \vec{R}_p) + \delta(\vec{R}_n, 0)\left[F_{ab}(0)(aa|bb) + F_{ba}(0)(ab|ab)\right] = E F_{ab}(\vec{R}_n)$$

$$\sum_p \left[\mathscr{E}_a(\vec{R}_p) + \mathscr{E}_b(\vec{R}_p)\right] F_{ba}(\vec{R}_n + \vec{R}_p) + \delta(\vec{R}_n, 0)\left[F_{ba}(0)(aa|bb) + F_{ab}(0)(ab|ab)\right] = E F_{ba}(\vec{R}_n)$$

(3. 20)

The secular equations break into two parts, one connecting the F_{aa} and F_{bb} type two-electron wave functions and the other connecting the F_{ab} and F_{ba} types. This splitting is due to our approximation in considering interactions of electrons only when they are on the same lattice site. In what follows we make use of these abbreviations

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

$$V_o = (aa|aa) = (bb|bb) = \int a(\vec{r}_1) \, a(\vec{r}_2) \, g_{12} \, a(\vec{r}_1) \, a(\vec{r}_2) \, d\tau_1 \, d\tau_2$$

$$J = (ab|ab) = \int a(\vec{r}_1) \, b(\vec{r}_2) \, g_{12} \, a(\vec{r}_1) \, b(\vec{r}_2) \, d\tau_1 \, d\tau_2$$

$$K = (aa|bb) = \int a(\vec{r}_1) \, a(\vec{r}_2) \, g_{12} \, a(\vec{r}_1) \, b(\vec{r}_2) \, d\tau_1 \, d\tau_2$$

We also make the assumptions that only those Fourier coefficients of the one-electron energy that represent nearest neighbor interactions are non zero. We call $\mathscr{E}_1$ the interaction between an x-like Wannier function and one displaced a unit translation in the x direction. We call $\mathscr{E}_2$ the interaction between an x-like Wannier function and one displaced a unit displacement in the y direction. A new feature comes into this calculation of the energies of the two-electron functions associated with the degenerate bands. In this case it sometimes occurs that the symmetry of the wave function is not sufficien. to determine whether the wave function is a singlet or a triplet. When this is the case there can be both a singlet and a triplet of the same symmetry. Instead of presenting a detailed discussion of the many symmetries and multiplicites we present the results in Table 3-3. The arguments that go into deriving the tabulated results are exactly analogous to those already presented for the non-degenerate band. The first column (I) represents the multiplicity of the state. The second column (II) gives the symmetry. The third column (III) tells whether the wave function comes from the F_{aa} type secular equations or the F_{ab} type secular equations (see Eq. (3.20)). In the fourth column (IV), there is listed the secular determ nant and in the final column (V) is listed the approximate eigenvalues for $\mathscr{E}_1$ and $\mathscr{E}_2$ small. In this column we have used the abbreviation that $\mathscr{E}_1 = c \, \mathscr{E}_2$.

For the case of a two-electron wave function drawn from two degenerate bands it is not possible to draw an unambiguous conclusion as to whether the triplet or the singlet lies lower as one can see from Table 3-3. Of those states in which one electron is in each band (F_{ab} type), it is clear that the lowest state of A_2 symmetry is a triplet lower than any other state of the F_{ab} type. Of the wave functions in which both electrons are in the same band (F_{aa} type), the lowest state is a singlet of B_1 symmetry. As to the competition between these two, the lowest one will be determined by the actual values of the parameters involved. Either one of these two could lie lower. Thus we see that in the case of non-degenerate bands the singlet lies lower whereas in the case of degenerate bands it is possible that the triplet may lie lower.

References

1. J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1953, p. 6.

2. H. Statz, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1953, p. 23; April 15, 1953, p. 20.

Energies for two-electron states arising from
degenerate bands in a square lattice

I	II	III	IV	V
singlet	A_1	F_{aa}	$E^4 - (V_0 + J)E^3 - 16(\mathcal{E}_1^2 + \mathcal{E}_2^2)E^2 + 8(V_0 + J)(\mathcal{E}_1^2 + \mathcal{E}_2^2)E$ $+ 64(\mathcal{E}_1^2 - \mathcal{E}_2^2)^2 = 0$	$E = V_0 + J \ldots$ $E = -\dfrac{8\mathcal{E}_1^2(1-c^2)^2}{(V_0+J)(1+c^2)}\ldots$ $E = \pm 2\sqrt{2}\sqrt{\mathcal{E}_1^2 + \mathcal{E}_2^2} - \mathcal{E}_1^2\dfrac{16c^2}{(V_0+J)(1+c^2)}\ldots$
singlet	A_2	F_{aa}	$E = 0$	$E = 0$
singlet	B_1	F_{aa}	$E^4 - (V_0 - J)E^3 - 16(\mathcal{E}_1^2 + \mathcal{E}_2^2)E^2 + 8(V_0 - J)(\mathcal{E}_1^2 + \mathcal{E}_2^2)E$ $+ 64(\mathcal{E}_1^2 - \mathcal{E}_2^2)^2 = 0$	$E = V_0 - J \ldots$ $E = -\dfrac{8\mathcal{E}_1^2(1-c^2)^2}{(V_0-J)(1+c^2)}\ldots$ $E = \pm 2\sqrt{2}\sqrt{\mathcal{E}_1^2 + \mathcal{E}_2^2} - \mathcal{E}_1^2\dfrac{16c^2}{(V_0-J)(1+c^2)}\ldots$
singlet	B_2	F_{aa}	$E = 0$	$E = 0$
triplet	E	F_{aa}	$E = \pm 2\sqrt{2}\,\mathcal{E}_1$ $E = \pm 2\sqrt{2}\,\mathcal{E}_2$	$E = \pm 2\sqrt{2}\,\mathcal{E}_1$ $E = \pm 2\sqrt{2}\,\mathcal{E}_2$
singlet	A_1	F_{ab}	$E = 0$	$E = 0$
singlet	A_2	F_{ab}	$E = 0$	$E = 0$
triplet	A_2	F_{ab}	$E^3 - E^2(K - J) - 8(\mathcal{E}_1 + \mathcal{E}_2)E + 4(\mathcal{E}_1 + \mathcal{E}_2)^2(K - J) = 0$	$E = K - J + \ldots$ $E = \pm 2(\mathcal{E}_1 + \mathcal{E}_2) - \dfrac{2}{K - J}(\mathcal{E}_1 + \mathcal{E}_2)^2 + \ldots$
singlet	B_1	F_{ab}	$E = 0$	$E = 0$
triplet	B_2	F_{ab}	$E = 0$	$E = 0$
singlet	B_2	F_{ab}	$E^3 - E^2(K + J) - 8(\mathcal{E}_1 + \mathcal{E}_2)E + 4(\mathcal{E}_1 + \mathcal{E}_2)^2(K + J) = 0$	$E = K + J + \ldots$ $E = \pm 2(\mathcal{E}_1 + \mathcal{E}_2) - \dfrac{2}{K + J}(\mathcal{E}_1 + \mathcal{E}_2)^2 + \ldots$
singlet	E	F_{ab}	$E = \pm\sqrt{2}(\mathcal{E}_1 + \mathcal{E}_2)$	$E = \pm\sqrt{2}(\mathcal{E}_1 + \mathcal{E}_2)$
triplet	E	F_{ab}	$E = \pm\sqrt{2}(\mathcal{E}_1 + \mathcal{E}_2)$	$E = \pm\sqrt{2}(\mathcal{E}_1 + \mathcal{E}_2)$

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

References (con'd)

3. G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1953, p. 31.

4. F. Seitz, Ann. Math. 37, 17 (1936).

5. L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).

6. G. F. Koster, Phys. Rev. 89, 67 (1953).

G. F. Koster and H. Statz

4. A SYSTEM OF TWO p ELECTRONS

In connection with the work on the two-electron example of ferromagnetism developed by other members of the Group,[1] there occurred a question regarding the energy levels of a system of two Ni atoms as a function of the internuclear distance; the reason is that the properties of the pair of atoms might be supposed to give information about the ferromagnetic substance in bulk.

In order to obtain qualitative information about this system, particularly about the multiplicity of the lowest lying state, the problem was simplified several steps as follows. A Ni atom which has one hole is 3d orbits is first reduced to an atom with a hole in p orbits, because both d and p levels give rise to degenerate bands. A hole in p orbits behaves qualitatively similar to an electron in p orbits. Furthermore, the Gaussian type of wave functions may be enough to give the qualitative information.

After these considerations, now the energy levels of a system of two atoms each having one p electron is being calculated using Gaussian wave functions, as a function of internuclear distance, and taking into account the configuration interaction.

Reference

1. H. Statz, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1953, p. 23; G. F. Koster, ibid. p. 31; J. C. Slater, April 15, 1953, p. 6.

R. Kikuchi

5. SPIN OPERATOR METHOD -- APPLICATION TO CONFIGURATION INTERACTION

A detailed account of an operator method of constructing eigenfunctions of S^2 was presented in the last Progress Report. The application of this technique to configuration interaction has proved rather successful and some of the details of its use will be given here. The following remarks will be largely confined to the treatment of the Mn^{++}—$O^=$—Mn^{++} model of antiferromagnetism discussed elsewhere in the present Progress Report.

It was shown in the April 15 Quarterly Progress Report that there exists an operator O when operating on a 2N electron determinant whose M_s value is zero, produces a linear combination of 2N electron determinants such that the resulting state is a singlet. The only condition imposed was that all the one-electron spatial orbitals be distinct, but not necessarily orthonormal. It was also pointed out in that Report that this operator method could be used to set up the matrix components of the Hamiltonian between singlets corresponding to different configurations. Suppose p_1 is a product function of space-spin orbitals

$$p_1 = u_1(1) \, \alpha(1) \, u_2(2) \, \alpha(2) \, \ldots \, u_N(N) \, \alpha(N) \, u_{N+1}(N+1) \, \beta(N+1) \, \ldots \, u_{2N}(2N) \, \beta(2N) \quad (5.1)$$

of total $M_s = 0$. Then one of the singlet states that can be formed from this collection of spatial orbitals is

$$\psi = AOp_1 \tag{5.2}$$

where O is the spin operator and A is the antisymmetrizing operator. The matrix component of the energy between two configurations for this particular type of singlet is

$$\langle \psi_1 \, H \, \psi_2 \rangle = \langle AOp_1 \, H \, AOp_2 \rangle \tag{5.3}$$

We now make use of the following properties of the spin operator O: (1) O commutes with a spin-free Hamiltonian. (2) O commutes with the antisymmetrizing operator A. (3) The square of O is equal to a constant times O. These properties allow one to write Eq. (5.3) as

$$\langle \psi_1 |H| \psi_2 \rangle = (N+1)^{1/2} \langle A^{(2N)} \, O^{(2N)} \, p_1 |H| p_2 \rangle \tag{5.4}$$

where p_1 and p_2 are spin product functions corresponding to different configurations and $A^{(2N)}$ and $O^{(2N)}$ signify that these operators are functions of the coordinates of all of the electrons.

In the ground configuration of the Mn^{++}—$O^=$—Mn^{++} system the orbitals con-

sidered are the five Mn 3d orbitals each singly occupied and the oxygen 2p orbitals which are assumed to hold six electrons. Thus we have a sixteen-electron system but only thirteen distinct orbitals. The object of these remarks is to generalize the spin operator O in order to handle systems composed of spatial orbitals all of which are not distinct. By doing this we will be able to cast matrix elements in the convenient form given in Eq. (5.4).

In the investigation of the Mn^{++}—$O^{=}$—Mn^{++} system the singlet considered for the ground configuration was formed by combining two $S = 5/2$ states made up from the Mn 3d orbitals to give a resultant ten-electron singlet. The remaining six electrons were assigned to the three 2p oxygen orbitals. In terms of the spin operator this sixteen-electron singlet is written

$$\Psi = A^{(16)} \left[u_1(1)\, \alpha(1)\, u_1(2)\, \beta(2) \ldots u_3(5)\, \alpha(5)\, u_3(6)\, \beta(6) \cdot O^{(10)} \left\{ u_4(7)\, \alpha(7)\, u_5(8)\, \alpha(8) \right. \right.$$
$$\left. \left. u_6(9)\, \alpha(9) \ldots u_8(11)\, \alpha(11)\, u_9(12)\, \beta(12)\, u_{10}(13)\, \beta(13) \ldots u_{13}(16)\, \beta(16) \right\} \right] \tag{5.5}$$

where u_1, u_2, and u_3 represent the 2p functions and u_4 through u_8 are the 3d functions on one Mn^{++} ion and u_9 through u_{13} are the 3d orbitals on the other Mn^{++} ion. An essential point appears here; that is the ten-electron spin operator $O^{(10)}$ does not commute with the sixteen-electron antisymmetrizing operator $A^{(16)}$. Therefore, unless this singlet can be set up using the full sixteen-electron spin operator $O^{(16)}$, the matrix components cannot be handled as in (5.4).

Consider a 2N electron system with $2(N - n)$ distinct orbitals which will be kept singly occupied and n distinct orbitals which will be doubly occupied. The orbitals may be catalogued in the following manner

$$\underbrace{u_{1_A}\ u_{2_A}\ \cdots\ u_{n_A}}_{\text{Group I}_A} \qquad \underbrace{u_{n+1_A}\ \cdots\ u_{N_A}}_{\text{Group II}_A}$$

$$\underbrace{u_{1_B}\ u_{2_B}\ \cdots\ u_{n_B}}_{\text{Group I}_B} \qquad \underbrace{u_{n+1_B}\ \cdots\ u_{N_B}}_{\text{Group II}_B} \tag{5.6}$$

If all of the functions were distinct, the 2N electron singlet under discussion would be written

$$\psi = A^{(2N)} O^{(2N)} \left\{ u_{1_A}(1)\, \alpha(1) \ldots u_{N_A}(N)\, \alpha(N)\, u_{1_B}(N+1)\, \beta(N+1) \ldots u_{N_B}(2N)\, \beta(2N) \right\} \tag{5.7}$$

(SPIN OPERATOR METHOD -- APPLICATION TO CONFIGURATION INTERACTION)

Suppose now we set u_{j_A} equal to u_{j_B} for j going from 1 to n in the singlet given in (5.7). Such a change cannot affect the multiplicity of the total wave function. However, many of the determinants which comprise (5.7) will vanish as a result of assigning the same spin to orbitals whose spatial parts are now assumed identical. Of the non-vanishing determinants, many will differ from others merely by interchanges of rows and hence these determinants can be combined. The net result of this change of spatial orbitals is that the normalization of the resultant singlet is destroyed. $O^{(2N)}$ must be modified so that the normalization can be preserved under such a change.

It can be shown that the necessary modification of $O^{(2N)}$ is to multiply it by a constant factor which depends only on the total number of electrons, 2N, and the number of identical orbitals, n. This factor is

$$\left[\sum_{k=0}^{n} \frac{n! \, (N-k)!}{(n-k)! \, N!} \right]^{-1/2} \tag{5.8}$$

Once the matrix elements have been reduced to the form of Eq. (5.4), $O^{(2N)}$ can be replaced by an equivalent operator for the purpose of taking the matrix component. The equivalent operator is obtained by omitting entirely the one-electron operators S_i^{+}, S_j^{-} where i and j refer to electrons occupying an orbital which is doubly filled. More precisely, this operator is $O^{2(N-n)}$ and it operates only on the spin coordinates of the electrons in groups II_A and II_B. This is a valuable result as it materially reduces the amount of work necessary to find the matrix components. Therefore, in the case of Mn—O—Mn the matrix component of the energy between the singlets corresponding to the ith and j^{th} configurations can be expressed as

$$\langle \psi_i |H| \psi_j \rangle = (N-n+1)^{1/2} \langle A^{(16)} O^{(10)} p_i |H| p_j \rangle \tag{5.9}$$

where N is 8 and n is equal to the number of doubly filled orbitals which is three.

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6. ANTIFERROMAGNETISM

At the present time attempts to give a quantum mechanical description of anti-ferromagnetism have been largely restricted to the treatment of simple models which supposedly would show a preference for spins to be oriented antiferromagnetically. A configuration interaction treatment of the $Mn^{++}-O^{=}-Mn^{++}$ system is reported here. The Mn—Mn distance as determined by x-ray scattering is 4.426 A^{o}[1] and it seems unlikely that the Mn 3d orbitals located about centers this distance apart would overlap appreciably. This overlap was neglected in this investigation. By considering excited configurations in which there is an unpaired spin on the oxygen, a spin dependent coupling will appear which causes the non-overlapping charge distributions associated with the Mn ions to interact through the oxygen. This is commonly referred to as super-exchange interaction.[2] The object of this work was to examine the nature of this coupling to determine whether it would tend to orient the spins of the Mn electrons ferromagnetically or non-magnetically.

The ground configuration was taken to be two Mn^{++} ions and an $O^{=}$ ion. The Mn^{++} ion has five 3d electrons outside closed shells and the $O^{=}$ ion was taken to have a rare gas configuration. The excited configurations considered were those obtained by allowing an electron in an orbital associated with the $O^{=}$ ion to occupy one of the Mn 3d orbitals. The only symmetry considered in the work was of the $\sum_{g}^{+}$ type as the ground state has this symmetry.

The one-electron functions used were assumed to be localized and orthonormal although the results obtained are independent of their exact nature. Table 6-1 shows the assignment of electrons for the various configurations. The Mn 3d orbitals are denoted by: $m_1 = 2 (\delta_+)$, $m_1 = 1 (\pi_+)$, $m_1 = 0 (\sigma)$, $m_1 = -1 (\pi_-)$, and $m_1 = -2 (\delta_-)$. The oxygen orbitals are $m_1 = 1 (P_+)$, $m_1 = 0 (P_o)$, $m_1 = -1 (P_-)$.

The states of maximum multiplicity, $S = 5$, for each configuration and the corresponding secular equation was set up. The energy of the lowest $S = 5$ state was compared with the energy of the lowest singlet found by constructing one particular singlet for each configuration and examining the resulting secular equation. Let us consider the choice of this singlet state.

For each configuration there are ten singly occupied orbitals and, therefore, 42 orthogonal singlets. From neutron diffraction studies of MnO, it is thought that the Mn^{++} ions can be divided into two sublattices each sublattice being ferromagnetically coupled:[1] the singlet state most closely resembling this situation is that formed by combining the two sublattices which are separately in a state of maximum spin to give a resultant singlet for the entire system. The analogue of this picture in the model being considered here is for the two Mn ions to be each in a state of maximum multiplicity and for these two $S = 5/2$ systems to combine to give a singlet for the ground configuration. The singlet for each excited configuration was formed by the combination of two $S = 5/2$ systems. As it is only possible to form one independent singlet in this manner,

Table 6-1

	δ_+	δ_-	π_+	π_-	σ	P_0	P_+	P_-	σ'	π_-'	π_+'	δ_-'	δ_+'
ψ_1	1	1	1	1	1	2	2	2	1	1	1	1	1
ψ_2	1	2	1	1	1	2	2	1	1	1	1	1	1
ψ_3	1	1	1	1	1	2	2	1	1	1	1	2	1
ψ_4	1	1	1	2	1	2	2	1	1	1	1	1	1
ψ_5	1	1	1	1	1	2	2	1	1	2	1	1	1
ψ_6	1	1	2	1	1	2	1	2	1	1	1	1	1
ψ_7	1	1	1	1	1	2	1	2	1	1	2	1	1
ψ_8	2	1	1	1	1	2	1	2	1	1	1	1	1
ψ_9	1	1	1	1	1	2	1	2	1	1	1	1	2
ψ_{10}	1	1	1	1	2	1	2	2	1	1	1	1	1
ψ_{11}	1	1	1	1	1	1	2	2	2	1	1	1	1

for each configuration one $S = 5$ and one $S = 0$ state was considered.

The states which are even with respect to a reflection in a plane perpendicular to the symmetry axis and passing through the oxygen are:

$$\Phi_0^g = \psi_1$$

$$\Phi_1^g = \psi_2 + \psi_3$$

$$\Phi_2^g = \psi_4 + \psi_5$$

$$\Phi_3^g = \psi_6 + \psi_7 \qquad (6.1)$$

$$\Phi_4^g = \psi_8 + \psi_9$$

$$\Phi_5^g = \psi_{10} + \psi_{11}$$

From these six states the states which have the + symmetry with respect to reflection in a plane containing the symmetry axis of the model can be formed. These four states are:

$$\phi_1 = \Phi_0^g = \psi_1$$

$$\phi_2 = \Phi_1^g + \Phi_4^g = \psi_2 + \psi_3 + \psi_8 + \psi_9 \qquad (6.2)$$

$$\phi_3 = \bullet_2{}^g + \bullet_3{}^g = \psi_4 + \psi_5 + \psi_6 + \psi_7$$

$$\phi_4 = \bullet_5{}^g = \psi_{10} + \psi_{11}$$

(6. 2) con'd.

The $S = 5$ and $S = 0$ states corresponding to these four $\sum_g^+$ states were set up and the corresponding secular equations written down. The $S = 5$ states were handled by conventional methods in that the states $\psi_i(S = 5)$ are just a single determinant. The singlet states $\psi_i(S = 0)$ are, however, much more complicated as these singlets are each expressed as a linear combination of 252 determinants. It would be an enormous task to compute the matrix components of the energy for these states by the customary procedures. These matrix components were found by the spin operator method reported in the preceding Quarterly Progress Report. The essence of this method is that one can construct a state of definite multiplicity by operating on a single determinant of one-electron space-spin orbitals with an operator which is essentially a polynomial the elements of which are step-up and step-down spin operators taken to various powers. This operator has the properties that it is hermetian, it commutes with a spin free Hamiltonian, it commutes with the S^2 operator, it commutes with the antisymmetrizing operator, and its square is equal to a constant times itself. These properties allow one to use the operator to take matrix components of the Hamiltonain between singlets corresponding to all configurations.[3] Some of the details involved are given in another section of the current Progress Report.

In terms of the spin operator O and the antisymmetrizing operator A, we can write the four $^1\sum_g^+$ states as

$$\phi_1(S = 0) = AOp_1$$

$$\phi_2(S = 0) = AO(p_2 + p_3 + p_8 + p_9)$$

$$\phi_3(S = 0) = AO(p_4 + p_5 + p_6 + p_7)$$

$$\phi_4(S = 0) = AO(p_{10} + p_{11})$$

(6. 3)

where the p_i are spin product functions referring to the various configurations.

$$p_1 = \delta_+(1)\alpha(1)\,\delta_-(2)\alpha(2)\,\pi_+(3)\alpha(3)\,\pi_-(4)\alpha(4)\,\sigma(5)\alpha(5)\,P_o(6)\alpha(6)\,P_o(7)\beta(7)\,P_+(8)\alpha(8)\,P_+(9)\beta(9)$$

$$P_-(10)\alpha(10)\,P_-(11)\beta(11)\,\sigma'(12)\beta(12)\,\pi_-'(13)\beta(13)\,\pi_+'(14)\beta(14)\,\delta_-'(15)\beta(15)\,\delta_+'(16)\beta(16)$$

(6. 4)

$$P_2 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,\delta_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.5}$$

$$P_3 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,\delta_-{}'(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.6}$$

$$P_4 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,\pi_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.7}$$

$$P_5 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,\pi_-{}'(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.8}$$

$$P_6 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,\pi_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.9}$$

$$P_7 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,\pi_+{}'(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.10}$$

$$P_8 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,\delta_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.11}$$

$$P_9 = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,\delta_+{}'(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.12}$$

$$P_{10} = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,P_0(6)\,\alpha(6)\,\sigma(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.13}$$

$$P_{11} = \delta_+(1)\,\alpha(1)\,\ldots\,\sigma(5)\,\alpha(5)\,\sigma'(6)\,\alpha(6)\,P_0(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,P_-(10)\,\alpha(10)\,P_-(11)\,\beta(11)$$
$$\sigma'(12)\,\beta(12)\,\ldots\,\delta_+{}'(16)\,\beta(16) \tag{6.14}$$

The matrix elements of the energy for the $S = 0$ case are given as:

$$H_{11} = \gamma(AOp_1 |H| p_1) \tag{6.15}$$

$$H_{12} = \gamma(AOp_1 |H| p_2 + p_3 + p_8 + p_9) \tag{6.16}$$

$$H_{13} = \gamma(AOp_1 |H| p_4 + p_5 + p_6 + p_7) \tag{6.17}$$

$$H_{14} = \gamma(AOp_1 |H| p_{10} + p_{11}) \tag{6.18}$$

$$H_{22} = \gamma(AO \left\{p_2 + p_3 + p_8 + p_9\right\} |H| \left\{p_2 + p_3 + p_8 + p_9\right\}) \tag{6.19}$$

$$H_{23} = \gamma(AO \left\{p_2 + p_3 + p_8 + p_9\right\} |H| \left\{p_4 + p_5 + p_6 + p_7\right\}) \tag{6.20}$$

$$H_{24} = \gamma(AO \left\{p_2 + p_3 + p_8 + p_9\right\} |H| \left\{p_{10} + p_{11}\right\}) \tag{6.21}$$

$$H_{33} = \gamma(AO \left\{p_4 + p_5 + p_6 + p_7\right\} |H| \left\{p_4 + p_5 + p_6 + p_7\right\}) \tag{6.22}$$

$$H_{34} = \gamma(AO \left\{p_4 + p_5 + p_6 + p_7\right\} |H| \left\{p_{10} + p_{11}\right\}) \tag{6.23}$$

$$H_{44} = \gamma(AO \left\{p_{10} + p_{11}\right\} |H| \left\{p_{10} + p_{11}\right\}) \tag{6.24}$$

$$\gamma = \sqrt{6}$$

As an illustration of how the spin operator method works the element $\gamma(AOp_2/H/p_5)$ will be worked out in detail. All of the one-electron orbitals are ortho-normal and it has been assumed that there is no overlap between the orbitals localized about the two Mn ions. The spin operator used can be expressed as

$$O = \frac{1}{\gamma} \left\{ 1 + C_1 \sum_{j_A k_B}^{N} (S_{j_A}^- S_{k_B}^+) + C_2 \sum_{j_A > k_A}^{N} \sum_{m_B > n_B}^{N} (S_{j_A}^- S_{k_A}^- S_{m_B}^+ S_{n_B}^+) + \ldots \right\} \tag{6.25}$$

where

$$C_M = (-1)^M \frac{(N - M)!}{N! \, M!}$$

Since O is to operate on a spin product function, we may speak of the electrons as being distinguishable. Electrons 1, 3, 4, 5, and 10 comprise set A. Electrons 12, 13, 14, 15, and 16 make up set B. N is the number of electrons in set A or B and M is the number of β spins assigned to the electrons in set A or the number of α spins assigned to set B. Therefore, the term

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$$C_1 \sum_{j_A k_B}^{N} S_{j_A}^- S_{k_B}^+$$

in O means that j_A runs over the electrons in set A and k_B is to run over the electrons in set B. $(AOp_2/H/p_5)$ written out is

$$AO \left\{ \delta_+(1)\,\alpha(1)\,\delta_-(2)\,\alpha(2)\,\pi_+(3)\,\alpha(3)\,\pi_-(4)\,\alpha(4)\,\sigma(5)\,\alpha(5)\,P_o(6)\,\alpha(6)\,P_o(7)\,\beta(7)\,P_+(8)\,\alpha(8) \right.$$

$$P_+(9)\,\beta(9)\,\underline{P_-(10)\,\alpha(10)}\,\underline{\delta_-(11)\,\beta(11)}\,\sigma'(12)\,\beta(12)\,\pi_-'(13)\,\beta(13)\,\pi_+'(14)\,\beta(14)\,\delta_-'(15)$$

$$\beta(15)\,\delta_+'(16)\,\beta(16) \Big\}\, |H|\, \Big\{ \delta_+(1)\,\alpha(1)\,\delta_-(2)\,\alpha(2)\,\pi_+(3)\,\alpha(3)\,\pi_-(4)\,\alpha(4)\,\sigma(5)\,\alpha(5)\,P_o(6) \quad (6.26)$$

$$\alpha(6)\,P_o(7)\,\beta(7)\,P_+(8)\,\alpha(8)\,P_+(9)\,\beta(9)\,\underline{\pi_-'(10)\,\alpha(10)}\,\underline{P_-(11)\,\beta(11)}\,\sigma'(12)\,\beta(12)\,\pi_-'(13)$$

$$\beta(13)\,\pi_+'(14)\,\beta(14)\,\delta_-'(15)\,\beta(15)\,\delta_+'(16)\,\beta(16) \Big\}$$

where the orbitals which do not match are underlined.

The 1 from 0 combined with the 1 from A gives for a contribution

$$(P_-(10)\,\delta_-(11)\,|\,\pi_-'(10)\,P_-(11))$$

Due to the spatial orthogonality of the orbitals and due to spin orthogonality, the only contributing permutation from A that can be combined with the 1 from 0 is the identity permutation.

The term

$$C_1 \sum_{j_A k_B}^{N} S_{j_A}^- S_{k_B}^+$$

combined with the 1 from A makes no contribution due to spin orthogonality. The only term to give a non-zero result is $C_1\,S_{10}^-\,S_{13}^+$ which must be combined with $P_{10,\,13}^q$ $P_{10,\,13}^\sigma$ from A, the combination yielding

$$-C_1(\delta_-(11)\,P_-(13)\,|\,P_-(11)\,\pi_-'(13))$$

There will be no other terms entering into this matrix element. Therefore,

$$(AOp_2)|H|p_5) = (1 - C_1)(\delta_-(1)\,P_-(2)\,|\,P_-(1)\,\pi_-'(2) \qquad (6.27)$$

and C_1 is $-1/5$. By proceeding in exactly the same manner, all of the matrix elements of H for the $S = 0$ case can be set up.

Let the Hamiltonian matrix for the singlet states be denoted by H_0 and the Hamiltonian for the $S = 5$ states be H_5. Then we can set

$$H_0 = H_5 + D^{(4)} \tag{6.28}$$

The matrix D has the following form

$$D = \begin{vmatrix} O & O & O & O \\ O & D_{22} & D_{23} & O \\ O & D_{23} & D_{33} & O \\ O & O & O & D_{44} \end{vmatrix} \tag{6.29}$$

Now suppose ψ_0 is the eigenvector of H_0 corresponding to the lowest eigenvalue of H_0 which we shall call E_0. Then

$$(\psi_0|H|\psi_0) = (\psi_0|H_5|\psi_0) + (\psi_0|D|\psi_0) \tag{6.30}$$

or

$$E_0 = \mathscr{E}_{0,5} + D$$

If ψ_5 is the eigenvector of H_5 corresponding to the lowest eigenvalue E_5, then by the variational principle

$$(\psi_5|H_5|\psi_5) \leqslant (\psi_0|H_5|\psi_0) \tag{6.31}$$

or

$$E_5 \leqslant \mathscr{E}_{0,5}$$

Therefore,

$$E_0 \geqslant E_5 + D \tag{6.32}$$

$$(6.33)$$

We mean by ϕ_k for k = 1, 2, 3, 4, 5; δ_+, δ_-, π_+, π_-, σ respectively, and for k = 12, 13, 14, 15, 16; ϕ $\sigma' = $, π_+', δ_-', and δ_+' respectively. D_{33} is obtained by replacing $\delta_\pm$ by $\pi_\pm$ and $\delta_\pm'$ by $\pi_\pm'$ everywhere in D_{22} except when δ_+ and δ_+' occur as the result of a summation.

$$D_{23} = \frac{6}{5}(\delta_-(1)P_-(2)|P_-(1)\pi_-'(2)) + (\delta_-(1)P_0(2)|P_0(1)\pi_-'(2)) + (\delta_-(1)P_+(2)|P_+(1)\pi_-'(2))$$

$$+ \frac{6}{5}(\delta_-'(1)P_-(2)|P_-(1)\pi_-(2)) + (\delta_-'(1)P_0(2)|P_0(1)\pi_-(2)) + (\delta_-'(1)P_+(2)|P_+(1)\pi_-(2))$$

$$+ \frac{6}{5}(\delta_+(1)P_+(2)|P_+(1)\pi_+'(2)) + (\delta_+(1)P_0(2)|P_0(1)\pi_+'(2)) + (\delta_+(1)P_-(2)|P_-(1)\pi_+'(2))$$

$$+ \frac{6}{5}(\delta_+'(1)P_+(2)|P_+(1)\pi_+(2)) + (\delta_+'(1)P_0(2)|P_0(1)\pi_+(2)) + (\delta_+'(1)P_-(2)|P_-(1)\pi_+(2))$$

$$(6.34)$$

$$D_{44} = \frac{6}{5}\sum_{k=12}^{16}(\phi_k'(1)P_0(k)|P_0(1)\phi_k'(k)) + \frac{6}{5}\sum_{k=1}^{5}(\phi_k(1)P_0(k)|P_0(1)\phi_k(k))$$

$$+ \frac{12}{5}(\sigma(1)P_0(2)|P_0(1)\sigma'(2)) + 2(\sigma(1)P_+(2)|P_+(1)\sigma'(2)) + 2(\sigma(1)P_-(2)|P_-(1)\sigma'(2))$$

$$(6.35)$$

The principal parts of D_{22} and D_{33} are exchange integrals between the oxygen orbitals and the Mn orbitals; these integrals are all positive. The other integrals entering D_{22} and D_{33} are three-center integrals which cannot be of major import as they involve the orbitals of both Mn ions. Although these three-center integrals are by no

$$D_{22} = \frac{6}{5} \sum_{k=12}^{16} (\phi_k'(1) P_-(k) | P_-(1) \phi_k'(k)) + \frac{6}{5} \sum_{k=1}^{5} (\phi_k(1) P_-(k) | P_-(1) \phi_k(k))$$

$$+ \frac{6}{5} \sum_{k=12}^{16} (\phi_k'(1) P_+(k) | P_+(1) \phi_k'(k)) + \frac{6}{5} \sum_{k=1}^{5} (\phi_k(1) P_+(k) | P_+(1) \phi_k(k))$$

$$+ \frac{12}{5}(P_-(1) \delta_-(2) | \delta_-'(1) P_-(2)) + 2(\delta_-(1) P_0(2) | P_0(1) \delta_-'(2)) + 2(\delta_-(1) P_+(2) | P_+(1) \delta_-'(2))$$

$$+ \frac{12}{5}(P_+(1) \delta_+(2) | \delta_+'(1) P_+(2)) + 2(\delta_+(1) P_0(2) | P_0(1) \delta_+'(2)) + 2(\delta_+(1) P_-(2) | P_-(1) \delta_+'(2))$$

$$(6.33)$$

We mean by ϕ_k for $k = 1, 2, 3, 4, 5$; $\delta_+, \delta_-, \pi_+, \pi_-, \sigma$ respectively, and for $k = 12$, 13, 14, 15, 16; $\sigma', \pi_-', \pi_+', \delta_-'$, and δ_+' respectively. D_{33} is obtained by replacing δ_+ by π_+ and δ_+' by π_+' everywhere in D_{22} except when δ_+ and δ_+' occur as the result of a summation.

$$D_{23} = \frac{6}{5}(\delta_-(1) P_-(2) | P_-(1) \pi_-'(2)) + (\delta_-(1) P_0(2) | P_0(1) \pi_-'(2)) + (\delta_-(1) P_+(2) | P_+(1) \pi_-'(2))$$

$$+ \frac{6}{5}(\delta_-'(1) P_-(2) | P_-(1) \pi_-(2)) + (\delta_-'(1) P_0(2) | P_0(1) \pi_-(2)) + (\delta_-'(1) P_+(2) | P_+(1) \pi_-(2))$$

$$+ \frac{6}{5}(\delta_+(1) P_+(2) | P_+(1) \pi_+'(2)) + (\delta_+(1) P_0(2) | P_0(1) \pi_+'(2)) + (\delta_+(1) P_-(2) | P_-(1) \pi_+'(2))$$

$$+ \frac{6}{5}(\delta_+'(1) P_+(2) | P_+(1) \pi_+(2)) + (\delta_+'(1) P_0(2) | P_0(1) \pi_+(2)) + (\delta_+'(1) P_-(2) | P_-(1) \pi_+(2))$$

$$(6.34)$$

$$D_{44} = \frac{6}{5} \sum_{k=12}^{16} (\phi_k'(1) P_0(k) | P_0(1) \phi_k'(k) + \frac{6}{5} \sum_{k=1}^{5} (\phi_k(1) P_0(k) | P_0(1) \phi_k(k))$$

$$+ \frac{12}{5}(\sigma(1) P_0(2) | P_0(1) \sigma'(2)) + 2(\sigma(1) P_+(2) | P_+(1) \sigma'(2)) + 2(\sigma(1) P_-(2) | P_-(1) \sigma'(2))$$

$$(6.35)$$

The principal parts of D_{22} and D_{33} are exchange integrals between the oxygen orbitals and the Mn orbitals; these integrals are all positive. The other integrals entering D_{22} and D_{33} are three-center integrals which cannot be of major import as they involve the orbitals of both Mn ions. Although these three-center integrals are by no

means zero, they are overshadowed by the exchange integrals. Therefore D_{22} and D_{33} as well as D_{44} are positive. Since D_{44} is positive, if D is to have a negative eigenvalue it must come from the 2 x 2 secular equation involving D_{22}, D_{33}, and D_{23}. The secular polynomial coming from this part of D is

$$\lambda^2 - (D_{22} + D_{33})\lambda + D_{22}D_{33} - (D_{23})^2 = 0 \tag{6.36}$$

We can only have a negative root if $D_{22}D_{33} < (D_{23})^2$ since the sum of the roots is positive. By means of the same arguments which established the positive character of D_{22} and D_{33} we can see that D_{23} is less than either D_{22} or D_{33}. Therefore, the D matrix has no negative roots and consequently the energy of the lowest lying singlet state as found by this configuration interaction cannot lie below the lowest S = 5 state.

Up to this point configurations in which an electron on the oxygen ion goes into a 4s orbital on one of the Mn ions have not been included. The 4s orbitals are more extended than the 3d's and now we would have to admit exchange integrals between a 4s orbital localized about one Mn ion and the 3d orbitals localized about the other Mn. By examining the character of D_{22} and D_{33} it appears that the inclusion of these configurations could not lead to a lower lying singlet energy than that of the S = 5 states.

There is one quite definite conclusion which can be drawn from this investigation. Within the framework of the approximations made here it seems clear that when an electron is removed from the $O^=$ ion, leaving an unpaired spin on the oxygen, that this unpaired spin couples the non-overlapping charge densities on the Mn ions ferromagnetically. In view of this result, it appears likely that some other approach would be more profitable as an explanation of antiferromagnetism. Of course, it may well be that the singlet state considered here in no way resembles the antiferromagnetic state.

Before abandoning this simplified model there is one feature of the configuration interaction treatment that bears examination. That is the fact that this approach has placed all of the emphasis on the probability amplitudes of the various configurations, the energy being stationary with respect to the variation of these parameters. It is quite possible that the one-electron wave functions are really quite different for the singlet and S = 5 states. Furthermore, the use of orthogonal orbitals may force one to carry out a rather extensive configuration interaction to accurately describe the correct state of affairs. An investigation is being carried out at present using a mixture of orthogonal and non-orthogonal orbitals but considering only the ground configuration. The energy will be stationary with respect to variations of parameters in the one-electron functions and these functions will be determined separately for the states of different multiplicity. Preliminary results obtained for this approach have been encouraging.

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4. See for example, P. W. Anderson, Phys. Rev. <u>83</u>, 1260 (1951).

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7. AN EXTENSION OF HUND'S RULE

In the course of configuration interaction calculations with orthogonal orbitals it is sometimes interesting to know what the multiplicity is of the lowest state of some given class of states. In general it is impossible to answer this question without calculations. Under one set of circumstances it is possible to answer this question without any calculation. We know of Hund's rule of atomic spectra. Part of this rule states that of all the levels arising from a given spacial configuration the state of highest multiplicity lies lowest. A rule similar to this can be proved in general.

We imagine n distinct orthogonal orbitals u_1, u_2, ... u_n. We put one electron in each of these orbitals with either spin up or spin down. This gives rise to 2^n states. These states can be formed into states of definite multiplicity ranging from singlets (for n even) to states of multiplicity $n + 1$. (The presence of other orbitals which are doubly filled does not influence the validity of the following arguments and can be dropped from consideration.) We shall now show that there is no state that lies lower than the state of highest multiplicity. We lose no generality by restricting ourselves to all those states with the same z component of total spin. Of these only one corresponds to the state of highest multiplicity whereas for any other multiplicity there is in general more than one state of this multiplicity. Since states of different multiplicities cannot interact we are confronted with the problem of diagonalizing for each multiplicity the matrix of the Hamiltonian

$$H = \sum^{n} - \nabla_i^2 + f(i) + \sum_{i>j} g_{ij} \tag{7.1}$$

Here $f(i)$ is the one-electron potential and g_{ij} is the interelectronic Coulomb interaction. From the Dirac vector model[1] we know that for a given multiplicity the matrix of the Hamiltonian can be written down very simply.

$$\mathscr{H}_{\lambda\sigma} = \text{const.} + \sum_{ij} - J_{ij}(P_{ij})_{\lambda\sigma} \tag{7.2}$$

Here $\mathscr{H}_{\lambda\sigma}$ represents the Hamiltonian matrix and $(P_{ij})_{\lambda\sigma}$ are unitary matrices which represent the permutation of the spatial coordinates of electron i with those of electron j. J_{ij} is the customary exchange interaction $J_{ij} = \int u_i^*(1) u_j^*(1) g_{12} u_i(2) u_j(2) d\tau_1 d\tau_2$ which is greater than zero since it represents the interaction of a charge density with itself. We first consider the state of highest multiplicity. This has a Hamiltonian matrix which has only one row and one column. The matrices representing the permutations P_{ij} are matrices which have one row and one column. The matrix element in all these matrices is unity. Therefore the energy of the state of highest multiplicity is (apart from the constant in (7.2) which is the same for all states)

(AN EXTENSION OF HUND'S RULE)

$$E_{n+1} = - \sum J_{ij}$$

For any other multiplicity the matrices $(P_{ij})_{\lambda\sigma}$ are of larger size. Let us consider the diagonal energies of all the states of a given multiplicity. These energies are the diagonal elements of (7.2)

$$\mathscr{H}_{\sigma\sigma} = \sum_{ij} - J_{ij}(P_{ij})_{\sigma\sigma}$$

From the unitary nature of the matrices $(P_{ij})_{\lambda\sigma}$ we know that

$$(P_{ij})_{\sigma\sigma} \leqslant 1$$

Therefore it is clear from this fact and the fact that $J_{ij} > 0$ that

$$E_{n+1} = - \sum J_{ij} \leqslant \mathscr{H}_{\sigma\sigma} = \sum - J_{ij}(P_{ij})_{\sigma\sigma}$$

We have therefore proved that there is no state lower in energy than the state of highest multiplicity. One might ask if going through the process of diagonalizing the Hamiltonian matrix (7.2) will push some state lower than the state of highest multiplicity. This is not the case since in diagonalizing the matrix (7.2) we use a unitary transformation which does not destroy the unitary property of $(P_{ij})_{\lambda\sigma}$. This unitary property was all that was necessary to prove the theorem. In general, in order to get some state other than the state of highest multiplicity lying lowest it is necessary to take states into account which occupy the orbitals in a different manner possibly filling some of our n orbitals twice and leaving others empty.

Reference

1. P. A. M. Dirac, Proc. Roy. Soc. (London) A123, 714 (1939). For further references and a complete discussion of this method, see E. M. Corson, Perturbation Methods in the Quantum Mechanics of n Electron Systems (Hafner Publishing Company, New York, 1950).

G. F. Koster

8. ON THE O_2 GROUND ELECTRONIC WAVE FUNCTION

Microwave absorption measurements on $O^{16} O^{17}$ gas[1] exhibit a hyperfine structure. The observed spectrum agrees with that predicted on the basis of a perturbing Hamiltonian of the form $b\vec{I} \cdot \vec{S} + cI_z S_z$; $\vec{S}$ is the electron spin angular momentum of the molecule, and $\vec{I}$ is the O^{17} nuclear spin ($I = 5/2$). According to a theory by Frosch and Foley,[2, 1a] experimental values of

$$\langle P_2/r^3 \rangle = \int \left(\frac{3 \cos^2 \chi - 1}{2r^3} \right) \rho(\vec{r}) \, d\vec{r} \tag{8.1}$$

and $\rho(0)$ can be deduced from those of the parameters b and c. The angle between the internuclear axis (the z-axis) and the radius vector $\vec{r}$ from the O^{17} nucleus to an electron is denoted by χ, and $P_2(x) = (1/2)(3x^2 - 1)$. $\langle P_2/r^3 \rangle$ is the value of P_2/r^3 averaged with respect to the number density $\rho(\vec{r})$ of electrons of unpaired spin of the molecule, and $\rho(0)$ is the value of ρ at the O^{17} nucleus. In the following we compare the experimental values - 1.32 and 0.187 (in atomic units) of $\langle P_2/r^3 \rangle$ and $\rho(0)$, respectively, obtained by Miller and Townes[1, 1a] with values determined by Meckler's O_2 normal electronic wave function.[3]

$\langle P_2/r^3 \rangle$ may be defined more precisely as

$$\langle P_2/r^3 \rangle = \int \Psi^* \left(\sum_j \frac{P_2(\cos \chi_j)}{r_j^3} \right) 2s_{jz} \ \Psi \, d\tau \tag{8.2}$$

where $\vec{s}_j$ is the spin angular momentum of the jth electron measured in units of $\hbar$. The summation is over the N electrons of the molecule, and the integration is over the coordinates of all electrons (and is to include summation over spin coordinates). Ψ is a normalized electronic wave function, the solution of Schrödinger's equation for O_2 with a spin independent Hamiltonian and with fixed nuclei. Ψ is an eigenfunction of $\vec{S}^2$ and S_z with eigenvalues $S(S + 1)$ and $M_S = S$; $\vec{S} = \sum_j \vec{s}_j$. Upon integration over the coordinates of all electrons but one, and summation over all spin coordinates, (8.2) reduces to (8.1) in which $\rho(\vec{r})$ is defined by

$$\rho(\vec{r}) = N \int \Psi^*(X, X_2, \ldots, X_N) \, 2s_z \, \Psi(X, X_2, \ldots, X_N) \, d\sigma \, dX_2 \cdots dX_N \tag{8.3}$$

and satisfies $\int \rho(\vec{r}) \, d\vec{r} = \int \Psi^* 2S_z \Psi \, d\tau = 2S$. In case Ψ is expressed as a linear combination of determinants of orthonormal orbitals, $\rho(\vec{r})$ is a quadratic form in the orbitals, the cross-terms (overlap terms) arising from products of determinants differing by one orbital.

Quite generally $\rho(\vec{r})$ can be employed to find the expectation value of F:

$$\int \Psi^* F \Psi \, d\tau = \int f(\vec{r}) \, \rho(\vec{r}) \, d\vec{r}, \text{ where } F \text{ is an operator of the type } F = \sum_j f(\vec{r}_j) \, 2s_{jz}.$$

E. g.. in the theory of neutron-electron magnetic scattering[4] such an operator occurs with $f(\vec{r}) = \frac{1}{2} e^{i\vec{K} \cdot \vec{r}}$ where $\vec{K}$ is the neutron scattering vector.

The normal O_2 electronic level is a $^3\sum_g^-$. Meckler[3] approximates Ψ for this level by a linear combination of nine symmetry states of $^3\sum_g^-$ symmetry, each a linear combination of determinants of orthonormal orbitals, these orbitals being symmetry orbitals (LCAO molecular orbitals) from one configuration. We write Meckler's Ψ as

$$\Psi_M = \sum_{\mu=a}^{i} c_\mu \phi_\mu \tag{8.4}$$

where, in terms of the determinants specified in Table 8-1, the symmetry states ϕ_μ are given by

$$\phi_a = \frac{1}{2}(A + B - C - D)$$

$$\phi_b = \frac{1}{2}(B + C - A - D)$$

$$\phi_g = 2^{-3/2}(E + G - F - H + J + K - I - L) \tag{8.5}$$

$$\phi_h = 2^{-3/2}(F + G - E - H + I + K - J - L)$$

$$\phi_i = 2^{-3/2}(E + F - G - H + I + J - K - L)$$

and the one-determinant symmetry states ϕ_c, ϕ_d, ϕ_e, and ϕ_f. The coefficients c_μ as a function of R are given by Meckler.[3] The result of inserting (8.4) into (8.3) is, in terms of Meckler's symmetry orbitals (see Table 8-1),

$$\rho(\vec{r}) = C_1|\phi_0|^2 + C_2|x_0|^2 + C_3|x_\pm|^2 + C_4|\phi_\pm|^2 \tag{8.6}$$

where

$$C_1 = \alpha + \beta + \gamma - \delta$$

$$C_2 = \alpha + \beta - \gamma + \delta$$

$$C_3 = |c_a + c_b|^2 + 2|c_c|^2 + 2|c_e|^2 + \alpha - \beta + \gamma + \delta$$

Table 8-1

Determinants of the symmetry states*

	$2p\sigma_g$ ϕ_0	$2p\sigma_u$ χ_0	$2p\pi_g^+$ χ_+	$2p\pi_g^-$ χ_-	$2p\pi_u^+$ ϕ_+	$2p\pi_u^-$ ϕ_-
A	+ −	+ −	+	−	+	+
B	+ −	+ −	+	+	+	−
C	+ −	+ −	−	+	+	+
D	+ −	+ −	+	+	−	+
E	+	+	+	+ −	+ −	−
F	+	+	−	+ −	+ −	+
G	+	−	+	+ −	+ −	+
H	−	+	+	+ −	+ −	+
I	+	+	+ −	−	+	+ −
J	+	+	+ −	+	−	+ −
K	+	−	+ −	+	+	+ −
L	−	+	+ −	+	+	+ −
ϕ_c	+ −		+	+	+ −	+ −
ϕ_d	+ −		+ −	+ −	+	+
ϕ_e		+ −	+	+	+ −	+ −
ϕ_f		+ −	+ −	+ −	+	+

*The normalized determinants A, ..., ϕ_f with $M_S = 1$ are defined by the symmetry orbitals on the principal diagonal; these consist of filled $1s\sigma$ and $2s\sigma$ orbitals accounting for eight of the sixteen electrons, the remaining orbitals being specified by the above table, a + or − entry indicating that the space orbital is occupied by an electron with + or − spin. The space orbitals are labeled both in standard notation and in Meckler's notation. Meckler lists the nine $^3\sum_g^-$ symmetry states as eigenfunctions of S_z with eigenvalue $M_S = 0$; these yield the ϕ_μ when operated on by $(S_x + iS_y)/\sqrt{2}$.

$$C_4 = |c_a - c_b|^2 + 2|c_d|^2 + 2|c_f|^2 - \alpha + \beta + \gamma + \delta$$

$$\alpha = \frac{1}{4}|c_g - c_h + c_i|^2 \qquad \beta = \frac{1}{4}|- c_g + c_h + c_i|^2$$

$$\gamma = \frac{1}{4}|c_g + c_h - c_i|^2 \qquad \delta = \frac{1}{4}|c_g + c_h + c_i|^2$$

No overlap terms appear in ρ since all determinants involved differ by at least two or-bitals. This follows from the fact that no two space orbitals available for occupation outside the $1s\sigma$ and $2s\sigma$ filled shells are of the same symmetry. Values of the C's and their component parts are given in Table 8-2. At normal internuclear distance R = 2.28

Table 8-2

Values of the C's of Eq. (8.6) and their component parts for Meckler's O_2 normal $^3\Sigma_g^-$ electronic wave function. Note that $\sum_k C_k = 2.00$.

R	2.0	2.5	4.0	∞
C_1	- 0.0018	- 0.0036	0.4424	1/2
C_2	0.0024	0.0066	0.4425	1/2
C_3	1.9632	1.9183	0.5960	1/2
C_4	0.0361	0.0788	0.5181	1/2
α	0.0003	0.0013	0.2226	1/4
β	0.00002	0.0002	0.2202	1/4
γ	0.0060	0.0113	0.00004	0
δ	0.0081	0.0164	0.00008	0
$2|c_c|^2$	1.9400	1.8694	0.3804	1/4
$2|c_d|^2$	0.0216	0.0479	0.3208	1/4
$2|c_e|^2$	0.0084	0.0183	0.2129	1/4
$2|c_f|^2$	0.0007	0.0041	0.1998	1/4
$|c_a - c_b|^2$	0.00000	0.00004	0.00001	0
$|c_a + c_b|^2$	0.0005	0.0018	0.0001	0

the symmetry state ϕ_c, which corresponds to the molecular orbital solution for the normal O_2 molecule, predominates $(1 - |c_e|^2 \ll 1)$. The ρ for ϕ_c, which involves only $2p\pi_g$ orbitals χ_+, is not much different from the ρ for Ψ_M.

The value of $\langle P_2/r^3 \rangle$ calculated from ρ of Ψ_M at equilibrium internuclear separation is only about 27 percent of the experimental value - 1.32. When Meckler's orbitals in ρ are replaced by Hartree-Fock orbitals, the value of $\langle P_2/r^3 \rangle$ is about 90 percent of the experimental value. These values of $\langle P_2/r^3 \rangle$ are discussed in more detail in the next paragraph. It seems unlikely that if Hartree-Fock or other reasonable types of atomic orbitals were used in Meckler's calculation in place of his Gaussian-type orbitals, the C's of (8.6) would be significantly different. The value of $\langle P_2/r^3 \rangle$ will then depend largely on the types of orbitals. One expects that calculated values of the molecular energy and $\langle P_2/r^3 \rangle$ as a function of the atomic orbitals employed are not very well correlated, since $\langle P_2/r^3 \rangle$, but not the energy, is sensitive to values of the orbitals primarily in the vicinity of the O^{17} nucleus.

Let us consider first $\langle P_2/r^3 \rangle$ calculated for ϕ_c. We then have, in terms of the atomic orbitals $p_\pm$ about the O^{17} nucleus and $p_\pm'$ about the O^{16} nucleus

$$\langle P^2/r_3 \rangle = 2\int \frac{P_2}{r_3} |\chi_+|^2 \, d\vec{r} = (2 \cdot \frac{K^2}{2}) \, \Delta \left[1 - \epsilon_2(R) + \epsilon_3(R) \right] \qquad (8.7)$$

where

$$\Delta = \int (P_2/r^3) |p_\pm|^2 \, d\vec{r}$$

$$\epsilon_2(R) = 2\int (P_2/r^3) \, p_\pm^* \, p_\pm' \, d\vec{r} / \Delta \qquad (8.7')$$

$$\epsilon_3(R) = \int (P_2/r^3) |p_\pm'|^2 \, d\vec{r} / \Delta$$

and $K(R)$ is a normalization constant. Δ, which is $-\langle P_2/r^3 \rangle$ for an isolated O atom in its ground level $2p^4 \, ^3P$, is independent of R; it is negative, since the angular part of the integral is negative. For Meckler's Gaussian type p orbitals, Δ is - .304 and, if we ignore the other factors in (8.7), yields a theoretical value of $\langle P_2/r^3 \rangle$ only 23 percent of the experimental value. The theoretical value is increased somewhat by the remaining factors in (8.7). The contributions ϵ_2 and ϵ_3 involving the O^{16} orbital are small, and should decrease as R increases; in fact, for Meckler's orbitals and R = 2, $\epsilon_2 = - 0.03$ and $|\epsilon_3/\epsilon_2| \approx 0.04$, so that the factor $(1 - \epsilon_2 + \epsilon_3)$ increases* the theoretical

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*Actually ϵ_2 is the algebraic sum of three terms whose magnitudes for R = 2 are of the order ten times $|\epsilon_2|$, and it is not obvious that $|\epsilon_2|$ decreases monotonically with increasing R.

value by about 3 percent. K^2 for Meckler's orbitals has the values 1.25, 1.09, and 1.00 at R = 2.0, 2.5 and 4.0, respectively, so that the normalization of χ_+ increases the theoretical $\langle P_2/r^3 \rangle$ by about 15 percent at normal internuclear separation. The net result is that $\langle P_2/r^3 \rangle$ for the molecular orbital ground state of O$_2$ computed using Meckler's Gaussian type orbitals is still only 27 percent of the experimental value. Δ for a Hartree-Fock O orbital[1a] is 71 percent of the experimental $\langle P_2/r^3 \rangle$. If, however, one includes the other factors of (8.7), assuming these are unchanged in value, the discrepancy can be reduced to about 10 - 15 percent, perhaps even less when these factors are properly computed. The value of $\langle P_2/r^3 \rangle$ for Ψ_M is in slightly poorer agreement with experiment than that for ϕ_c. Now ρ involves integrals like (8.7) with the $2p\pi_u$, $2p\sigma_g$, and $2p\sigma_u$ orbitals. Since the latter integrals contribute to $\langle P_2/r^3 \rangle$ with small coefficients, they need not be investigated with great precision. For $2p\pi_u$ the integral differs from (8.7) in that K^2 is replaced by Meckler's $L^2 < 1$ and $\epsilon_3 \rightarrow -\epsilon_2$, and so is smaller in magnitude than (8.7). For $2p\sigma$ orbitals the sign of the integral is reversed, Δ being replaced by -2Δ. It is clear that $\langle P_2/r^3 \rangle_{\Psi_M}$ does not differ appreciably from $\langle P_2/r^3 \rangle_{\phi_c}$.

Let us next compare the experimental and calculated values of $\rho(0)$. For Ψ_M, $\rho(0)$ is very much less than the experimental value. This is not surprising, since only symmetry orbitals containing s orbitals have an appreciable density at the O^{17} nucleus, and Ψ_M involves s orbitals outside the filled 1sσ and 2sσ shells only in the 2pσ orbitals, and then only in virtue of the orthogonalization of the 2pσ to the 1sσ and 2sσ orbitals. Table 8-3 shows values of $\rho(0)$ for some atomic orbitals. Values of $\psi_{1s}(0)|^2$ and

Table 8-3
Values of $\rho(0)$ for some atomic orbitals

	Hydrogen-Like	O Hartree-Fock[5]	O$_2$ Meckler[3]
1s	0.318 Z^2	148.2	45.4
2s	0.318 $(Z/2)^2$	7.604	0.363

$|\psi_{2s}(0)|^2$ for Meckler's orbitals are smaller by factors 0.306 and 0.048, respectively, than the corresponding values for the Hartree-Fock O orbitals of Hartree, Hartree and Swirles.[5] Even when the latter replace Meckler's atomic orbitals in his symmetry orbitals, $\rho(0)$ is less than 0.001 for Ψ_M, smaller by a factor of about 100 than the experimental value 0.187. (We have neglected the reorthogonalization and renormalization that should be performed for these substituted atomic orbitals.)

Apparently the normal electronic state contains small admixtures of other symmetry states than those considered by Meckler, and these additional symmetry

states have large effects on $\rho(0)$. The situation can be clarified qualitatively to some degree. A rough criterion for the magnitude of the amplitude c_μ of a symmetry state is the sum of the energies of the component orbitals, the higher the energy, the smaller $|c_\mu|$. Only the σ orbitals of a symmetry state contribute appreciably to the density of unpaired spin in the vicinity of the O^{17} nucleus, since only these contain s orbitals. Thus, only symmetry states with unpaired σ orbitals can contribute effectively to $\rho(0)$. We can get some idea of the relative effects on $\rho(0)$ of various nsσ orbitals by noting that for hydrogen-like atomic orbitals $\psi_{n\ell}$, $|\psi_{n0}(0)/\psi_{10}(0)|^2 = n^{-3}$.

On the basis of these ideas we may expect that only symmetry states with low energy containing unpaired nsσ orbitals with small n give important contributions to $\rho(0)$. Examples of such are symmetry states which differ from one of the ϕ_μ in that a 1sσ or 2sσ orbital is replaced by an n$\ell\sigma$ of low n $\geqslant$ 2 and $\ell \neq 0$, or in that a 2pσ is replaced by an nsσ with small n $\geqslant$ 3. (Note that if the excited symmetry state is to have the same symmetry as a ϕ_μ and involve determinants which differ by only one orbital from thos of the ϕ_μ, the excited orbital must have the same symmetry as the unexcited. Also, a cross term in $\rho(\vec{r})$ vanishes at $\vec{r} = 0$, unless the orbitals which overlap are both sσ.)

Approximate wave functions in molecular theory are commonly determined by a variational procedure which makes the energy stationary. The result is that although the energy is insensitive to small variations in the wave function, other quantities, such as $\langle P_2/r^3 \rangle$ and $\rho(0)$, may be relatively quite sensitive. One should then not expect amounts of mixing of symmetry states which yield energies in satisfactory agreement with experiment to necessarily yield other molecular quantities in such satisfactory agreement; $\rho(0)$ is an example of such a quantity. On the same basis, types of atomic orbitals which lead to reasonable energies may lead to poor values of other molecular quantities; both $\langle P_2/r^3 \rangle$ and $\rho(0)$ are examples of such quantities.

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W. H. Kleiner

9. THE ETHANE MOLECULE

As indicated in the last Report, the severe restriction on the amount of configuration interaction to be considered necessitates an optimization of the molecular orbitals, a best choice of linear combinations of atomic orbitals. This problem is faced also by Dr. Kaplan in his treatment of the NH_3 molecule where even though quite a bit of configuration interaction is handled, the amount is still not enough to permit complete equivalence of all linear combinations of atomic orbitals. Roothaan[1] has given a procedure for determining best LCAO's for the case of a closed shell state, a single determinant many-electron wave function. His equations are the algebraic equivalent of the Hartree-Fock differential equations and are similarly characterized by the discouraging prospect of a self-consistent calculation. However, there is Whirlwind -- the high speed computer now of large capacity -- and Roothaan's procedure can be mechanized and performed by the machine so that it becomes a fast, repeatable routine. We wish to present a flow chart of the machine program now being developed but first we will re-express Roothaan's equations in a slightly modified form:

To begin with, there are the one-electron functions which are to be combined in the best possible ways. Let them be orthonormalized. Here we differ with Roothaan who did not require orthogonality. The lack of orthogonality leads to a more complicated type of determinantal equation to be solved and we see no point in adding this difficulty to the non-escapable one of self-consistency. We begin with a well-considered first guess to the molecular orbitals, an orthonormalized set. A general linear combination of these functions is still a general linear combination of the original atomic functions.

This original set of functions is denoted as v_μ and the number in the set by N. If there are 2n electrons in the system, we are to find n linear combinations of the v_μ's

$$\phi_i = \sum_\mu c_{i\mu} v_\mu$$

such that an antisymmetrized many-electron wave function formed with each ϕ_i doubly occupied will be associated with a minimum value of the energy. The expression for the energy is

$$E = 2 \sum_{\mu\nu} \rho_{\mu\nu} H_{\nu\mu} + \sum_{\mu\nu\lambda\sigma} \rho_{\mu\nu} G^{\mu\nu}_{\lambda\sigma} \rho_{\lambda\sigma}$$

where

$$H_{\mu\nu} = \int v_\mu^*(1) \left[-\nabla_1^2 + V(1) \right] v_\nu(1) d^3x_1$$

$$G_{\lambda\sigma}^{\mu\nu} = 2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)$$

$$(\mu\nu|\lambda\sigma) = \int v_\mu{}^*(1)\, v_\nu(1)\, \frac{2}{r_{12}}\, v_\lambda{}^*(2)\, v_\sigma(2)\, d^3x_1\, d^3x_2$$

$$\rho_{\mu\nu} = \sum_i c_{i\mu}^* \, c_{i\nu}$$

or in matrix notation

$$\rho = C^+ C \qquad (+ = \text{Hermitian adjoint})$$

and the orthonormalization of the ϕ_i's is implied by

$$CC^+ = 1$$

C is an n x N rectangular matrix. ρ is a square N x N. The n rows of C, which are the complex conjugates of the n columns of C, are the n lowest eigenvectors of the matrix

$$K_{\lambda\sigma} = H_{\lambda\sigma} + \sum_{\mu\nu} \rho_{\mu\nu}\, G_{\lambda\sigma}^{\mu\nu}$$

That is

$$KC^+ = \Lambda C^+ \qquad \Lambda \text{ diagonal}$$

We are to pick a ρ, form K, diagonalize it, selects its n lowest eigenvectors, form ρ, re-cycle. The thing to realize is that H and G do not change from cycle to cycle. They are the input to the machine, the data to be used over and over again. The flow chart is illustrated on p. 48.

The machine is to do matrix-vector multiplication (symbolized as ρG), matrix addition, matrix diagonalization, magnitude selection and comparison, and many cycles. Even with the type of factorization by symmetry discussed by Roothaan there is a lot to be stored in the machine, but the addition of more electrostatic storage tubes and a magnetic drum to Whirlwind has made for the pleasant atmosphere of a buyer's market in storage space.

The matrix diagonalization procedure, which is just a sub-routine in the whole self-consistent process, has been programmed and will exist as a separate routine in the Whirlwind library. The present program can handle up to a 31 x 31 real symmetric

(THE ETHANE MOLECULE)

Input stored

-48-
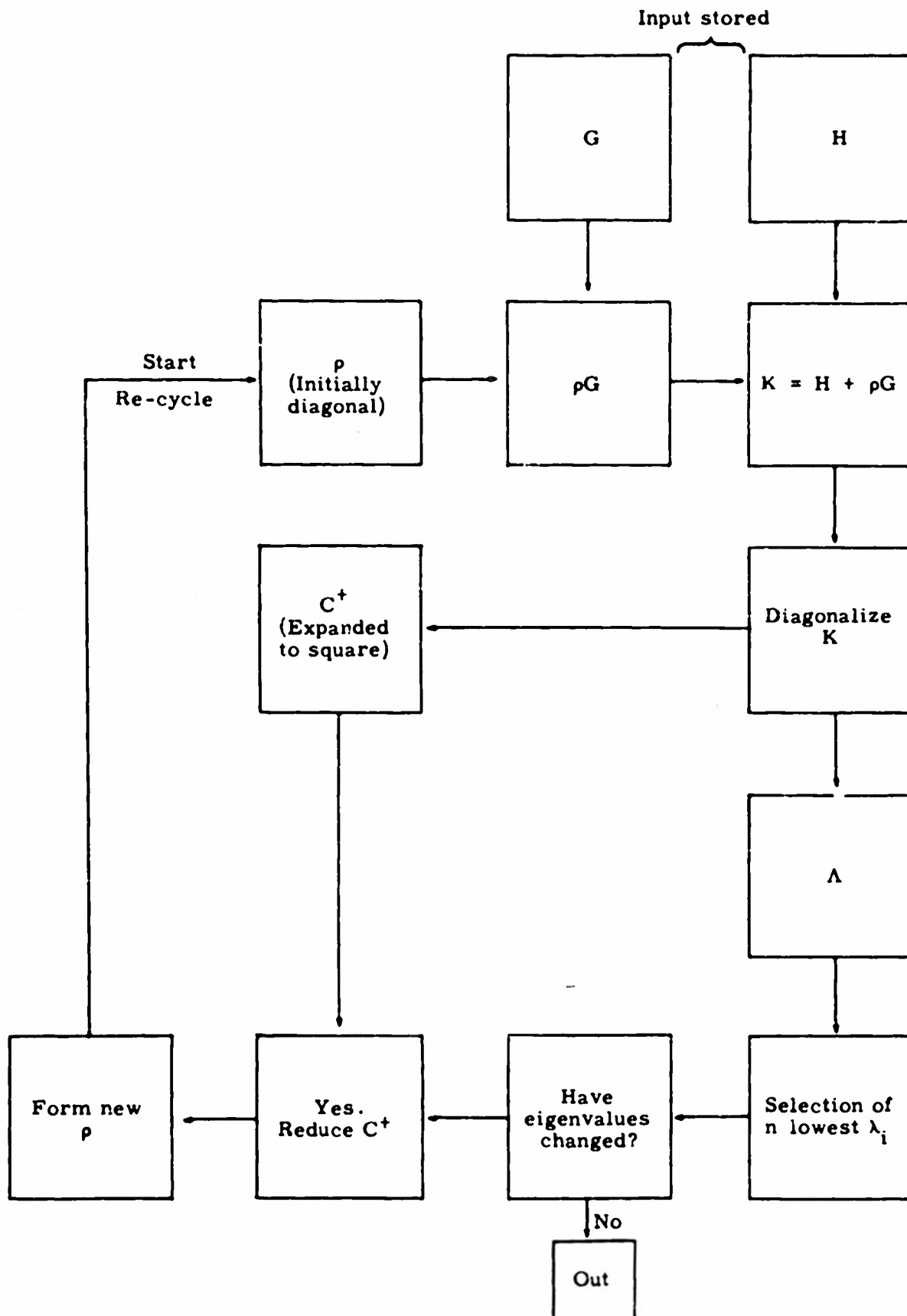
matrix and a 15 x 15 complex Hermitian matrix. The rest of the L.C.A.O. determination is now being programmed and will be first applied to the NH_3 molecule.

Alvin Meckler

10. LIMITED CONFIGURATION INTERACTION TREATMENT OF THE NH_3 MOLECULE

The calculation of matrix elements indicated in the last Progress Report is still underway. The matrix elements have been expressed in terms of "directed" molecular orbitals. Due to the symmetry properties of these one-electron functions, there are only thirty-five independent two-electron integrals and five independent one-electron integrals. Each of these integrals, however, is a combination of many similar type integrals involving atomic wave functions. At present the component atomic integrals are being expressed in a form necessary for the evaluation of their radial sub-integrals by I. B. M. machine methods.

H. Kaplan

11. THE WATER MOLECULE

The tabulation of the a_n's mentioned in the last Quarterly Progress Report is nearly complete. We now have the following ra_n's:

$$r = 0(.1)\ 1.2(.2)\ 4.0(.5)\ 7(1)\ 12$$

$$a = 1.4,\ 1.5,\ 1.6,\ 1.8,\ 2.0,\ 2.2,\ 2.6,\ 3.0,\ 4.0 \text{ and } 5.0$$

$$k = 1,\ 2$$

$$n = 0,\ 1,\ 2,\ 3,\ 4,\ 5 \text{ (for } k = 1\text{)}$$

$$n = 0,\ 1,\ 2,\ 3 \text{ (for } k = 2\text{)}.$$

The interelectronic interaction integrals involves terms of the form

$$\int_0^\infty \rho_{ab}(r_1) \left[\frac{1}{r_1^{\ell+1}} \int_0^{r_1} \rho_{cd}(r_2)\, r_2^{\ell}\, dr_2 + r_1^{\ell} \int_{r_1}^\infty \frac{\rho_{cd}(r_2)}{r_2^{\ell+1}}\, dr_2 \right] dr_1 \qquad (11.1)$$

These can be written as

$$\int_0^\infty \rho_{ab}(r_1) \left[\frac{1}{r_1^{\ell+1}} \int_0^{r_1} \rho_{cd}(r_2)\, r_2^{\ell} dr_2 \right] dr_1 + \int_0^\infty \rho_{cd}(r_1) \left[\frac{1}{r_1^{\ell+1}} \int_0^{r_1} \rho_{ab}(r_2)\, r_2^{\ell} dr_2 \right] dr_1$$

$$(11.2)$$

We shall call the quantity in square brackets in (11.2) the inner potential.

We have written and tested a program for computing the inner potential, where ρ_{ab} is the product of two radial probability amplitudes, for the I.B.M. Card Programmed Calculation. Our mesh is

$$r = 0(.0125)\ .05(.025)\ .2(.05)\ .6(.1)\ 1.2(.2)\ 4(.4)\ 10\ .$$

The program takes three minutes of machine time per integration. The results of this indefinite integral are printed and punched on cards ready for use in definite integrals. This program is now in use.

G. F. Koster

12. CONFIGURATION INTERACTION APPLIED TO THE HYDROGEN MOLECULE

Calculation of the several matrix elements discussed in the previous Progress Report is continuing. The odd one-electron function obtained from the Hartree equation containing an "average field" due to an electron in the even orbital has been determined. The kinetic energy and nuclear framework integrals appearing in the main diagonal element in which the electrons are in the odd orbital have been computed and there remains only the electron-electron interaction integrals to be found.

E. Callen

13. CONFIGURATION INTERACTION FOR THE FLUORINE MOLECULE[1]

In order to shorten the computation in the problem mentioned in the last Progress Report, it has been decided to use Slater-type atomic orbitals[2] instead of Hartree-Fock atomic orbitals. Work on the problem is proceeding along these lines.

References

1. The author is the holder of a Lilly Postdoctoral Fellowship from the National Research Council
2. J. C. Slater, Phys. Rev. $\underline{36}$, 57 (1930).

J. H. Barrett

14. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE

The introduction of a polarization effect by appropriate distortion of atomic orbitals has been studied along lines indicated in the previous Progress Report.[1] A special case of the proposed form:

$$\psi = \psi^o_{n\ell m}(1 + r^\nu Y^{m'}_{\ell'})$$ (14.1)

has been investigated quantitatively. In particular, we have chosen $n = 1$, $\ell = 0$, $m = 0$, $\ell' = 1$, $m' = 0$, and in addition we have provided for normalization and a "mixing coefficient", C. Thus our wave function is:

$$\psi = Ne^{-r}(1 + Cr^\nu \cos \theta)$$ (14.2)

where N = normalization constant and C, ν = variation parameters. (Unless otherwise stated, atomic units, a.u., are used throughout; a_o = unit of length = .529 x 10^{-8} cm, $e^2/2a_o$ = unit of energy = 13.53 e.v.)

Using (14.2) we have considered two types of perturbing fields: (1) a weak uniform field and (2) the field of a point charge a distance $R = 1.4$ a.u. away from the center of the unperturbed function.

Case (1)
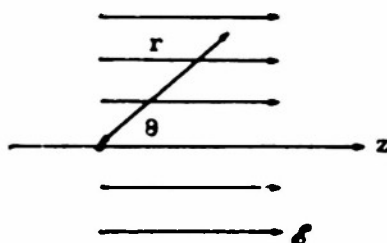
The Hamiltonian is:

$$H = H_o(\vec{r}) + H'(\vec{r}, \mathscr{E}) = -\nabla^2 - \frac{2}{r} + \mathscr{E} r \cos \theta$$

and $H'(\vec{r}, \mathscr{E})$ is considered to be small compared to H_o. We form:

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} = E_o - \frac{1}{2}a\mathscr{E}^2 + \dots$$ (14.3)

Our problem is really that of the second order Stark effect for the normal hydrogen atom -- which has been solved exactly[2] yielding a polarizability: $a = 2.25$ a.u. ($4.50 a_o^3$ in any other system of units). Using (14.2) and varying C and ν we obtain a minimum

of (14.3) for $C = -.724$, $\nu = 1.50$, giving $a = 2.25$ a.u. -- the correct value. For comparison we have used:

$$\psi_1 = N_1 \left[\psi_{1s} + C_1 \psi_{2pz} \right] \qquad \begin{cases} \psi_{1s} = \dfrac{1}{\sqrt{\pi}} \, e^{-r} \\[3mm] \psi_{2pz} = \dfrac{r \cos}{4\sqrt{2\pi}} \, e^{-r/2} \end{cases} \qquad (14.4)$$

Minimizing (14.3) with respect to C_1 we obtain $a = 1.48$ a.u. $(2.96 \, a_o^3)$ -- a value in error by 35 percent. The resulting expressions for ψ_1 and ψ are given below for Case (1). (We have separately normalized the angular dependent term of (14.2) so that the coefficient of the distortion terms are directly comparable):

$$\psi_1 = N_1 \left[\psi_{1s} - .995 \mathscr{E} \psi_{2pz} \right] \qquad N_1 = 1 - .495 \mathscr{E}^2$$

$$\psi = N \left[e^{-r} - 1.45 \mathscr{E} \left(\frac{r^{1.50} \cos\theta \, e^{-r}}{\sqrt{2.50}} \right) \right] \qquad N = .564 - .369 \mathscr{E}^2$$

It should be noted that for Case (1) (14.2) is just of the form:

$$\psi = \psi^o (1 + A H' + \dots)$$

which was suggested by Lennard-Jones[3] on the basis of an approximate treatment of second order perturbation theory. Also Slater and Kirkwood[4] have treated the normal hydrogen atom in a weak uniform field using a function of the form:
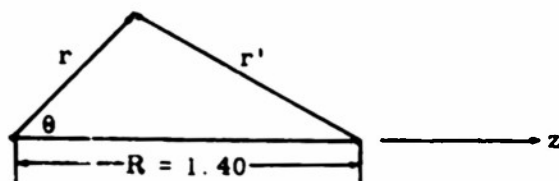
$$\psi = \psi^o (1 + H' R(r))$$

They obtained a differential equation for $R(r)$ and their resulting wave function was:

$$\psi = N \left[e^{-r} - 1 \mathscr{E} \left\{ \left(r + \frac{r^2}{2} \right) \cos\theta \, e^{-r} \right\} \right] \qquad N = .564 - .282 \mathscr{E}^2$$

and $a = 2.25 \, (4.50 \, a_o^3)$ - the exact value.

(NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE)

Case (2)

The Hamiltonian is:

$$H = H_o(\vec{r}) + H'(\vec{r}, R) = -\nabla^2 - \frac{2}{r} - \frac{2}{r'} + \frac{2}{R} \quad \begin{cases} \frac{1}{r'} = \frac{1}{R} \sum_k (\frac{r}{R})^k P_k(\cos \theta) \quad r < R \\[2ex] \frac{1}{r'} = \frac{1}{r} \sum_k (\frac{R}{r})^k P_k(\cos \theta) \quad r > R \end{cases}$$

Here we have a strong field case with $H'(\vec{r}, R)$ the same order of magnitude as $H_o(\vec{r})$. Again using (14.2) and minimizing the energy with respect to C and v for R = 1.40 we find C = .385, v = .65. For (14.4) we find C_1 = .109 and the respective functions are:

$$\psi = N \left[e^{-r} + .298 \left(\frac{r^{.65} \cos \theta \, e^{-r}}{\sqrt{.600}} \right) \right] \qquad N = .508$$

$$\psi_1 = N_1 \left[\psi_{1s} + .109 \, \psi_{2pz} \right] \qquad N_1 = .989$$

The exact solution of Schrödinger's equation for this potential is the hydrogen molecule ion with an energy at R = 1.40 of - 1.15 a. u. ψ gives an energy - .916 while ψ_1 gives - .809, the first representing a 20 percent greater value than the exact value for H_2^+ and the second a 30 percent greater value. However we are trying to solve a polarization problem and not the H_2^+ problem and thus we have not brought in the symmetry of the positive charges. Our calculation only shows that the wave function of (14.2) is more satisfactory than the case of (14.4) where we admix some $2p_z$ function with the 1s. The method of Slater and Kirdwood depends for the separability of their differential equation on linearity of H' in rectangular coordinates and spherical symmetry of ψ^o and appears not to be readily manageable for complicated cases.

As a further test of the function (14.2) the determinantal wave function for F^- is being set up using one-electron functions of the form (14.2) and determining C and v by minimizing the total energy.

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References (con'd)

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L. C. Allen

15. INTERSTITIAL DIFFUSION IN THE DIAMOND STRUCTURE

We wish to derive the diffusion coefficient for interstitial diffusion in the diamond structure by considering the elementary process of a transition of the interstitial ion from its original site to a neighboring one. We here consider only interstitial diffusion, for the case of infinite dilution of the diffusing substance, constant temperature, and absence of electric fields.

The diamond structure can be viewed as two interpenetrating face-centered cubic lattices, one having a parallel displacement of $(a/4, a/4, a/4)$ with respect to the other, a being the length of the side of the unit cube. The interstitial positions are found to have the diamond structure also, displaced by a body-centering translation from the original lattice. That is, if the carbon atoms are found at (000), F. C., and $(a/4, a/4, a/4)$, F. C., then the interstitial sites are located at $(a/2, a/2, a/2)$, F. C., and $(3a/4, 3a/4, 3a/4)$, F. C. The interstitial positions located with respect to it as as origin at $\vec{n}_1 = (a/4, a/4, a/4)$, $\vec{n}_2 = (a/4, -a/4, -a/4)$, $\vec{n}_3 = (-a/4, a/4, -a/4)$, $\vec{n}_4 = (-a/4, -a/4, a/4)$, and the interstitial position $(3a/4, 3a/4, 3a/4)$ has nearest-neighbor sites located with respect to it by the negatives of these displacements.

We assume that the transition probability is λ for a jump from one site to a nearest-neighbor site and O for any other jump. Then, if $P(\vec{r}_j, t)$ be the probability that site $\vec{r}_j$ is occupied by an interstitial ion at time t, we have

$$\dot{P}(\vec{r}_j, t) = -4\lambda P(\vec{r}_j, t) + \sum_{i=1}^{4} \lambda P(\vec{r}_j \pm \vec{n}_i, t)$$

where the upper sign holds if $\vec{r}_j$ is on the lattice containing $(a/2, a/2, a/2)$ and the lower sign holds for the other case. A Taylor's series expansion provides immediately the diffusion equation

$$\frac{\partial P}{\partial t}(\vec{r}, t) = \frac{\lambda a^2}{8} \nabla^2 P(\vec{r}, t) .$$

The diffusion constant is thus $D = \lambda a^2/8$.

The neglected terms in the equation for either lattice of ions are the third-derivative terms, but after averaging over both lattices the only terms which survive are the fourth and higher derivatives.

The assumption of infinite dilution of the diffusing substance can be relaxed somewhat, for it is found that if the probability of occupancy of target sites is considered the same diffusion equation results. The jumping probability λ will be a function of local concentration of diffusing substance, however, so the requirement of fairly high dilution would still hold.

<div align="right">H. C. Schweinler</div>

16. A STUDY OF $2Z_p$ IN ATOMS

The results of calculations of the effective nuclear charge for potential in an atom have been submitted to the Physical Review for publication.

A. J. Freeman

17. ATOMIC MULTIPLET SEPARATIONS

Atomic multiplet separations have been computed for atoms with uncompleted 3p and 3d shells. Simple analytic radial parts of the one-electron wave functions were assumed:

$$R_{3p} = C_8 r e^{-Z_2 r} + C_9 r^2 e^{-Z_3 r}$$

$$R_{3d} = C_{10} r^2 e^{-Z_4 r}$$

R_{3p} was obtained by taking a linear combination of single term expressions for the 2p and 3p radial functions. The single term expressions are given by Professor Slater[1] as:

$$r^{n^* - 1} e^{-\left[(Z - S)/n^*\right] r}$$

where Z is the atomic number and n^* and S are given by simple rules. C_8 and C_9 are determined from orthogonality conditions with the 2p radial function and by normalization. If one assumes the radial parts of the one-electron functions do not vary from multiplet to multiplet for a given configuration, a multiplet separation is given by a sum of Coulomb and exchange integrals. This sum may be expressed in terms of the $F^k(n, l; n', l')$ and $G^k(n', l; n', l')$ integrals.[2]

If orthonormal functions of the form,

$$R_{nl} = \sum_k C_k r^{n_k} e^{-Z_k r}$$

are used, the integrals may be written:

$$F^k(nl; n'l') = 2 \sum_{stuv} C_s C_t C_u C_v \, {}_k L^{n_s + n_t, \, n_u + n_v}(Z_s + Z_t, Z_u + Z_v)$$

where:

$$
{}_k L^{n_i n_j}(a, b) = \int_0^\infty \int_0^\infty r^{n_i} e^{-ar} \frac{r(a)^k}{r(b)^{k+1}} r'^{n_j} e^{-br'} r^2 r'^2 \, dr \, dr'
$$

$$
= (-1)^{n_i n_j} \frac{\partial^{n_i + n_j}}{\partial a^{n_i} \partial b^{n_j}} \, {}_k L^{00}(a, b)
$$

Table 17-1

	Multiplet Separation	Calculated Separation	Observed Separation
Silicon I $(3p)^2$	$^3P - {}^1D$	$10,285.5$ cm^{-1}	$6,198.66$ cm^{-1}
	$^1D - {}^1S$	$15,428.2$	$9,095.43$
Phosphorus I $(3p)^3$	$^4S - {}^2D$	$17,179.0$	$11,369.1$
	$^2D - {}^2P$	$11,452.6$	$7,366.1$
Potassium V $(3p)^3$	$^4S - {}^2D$	$20,914.6$	$24,118.5$
	$^4S - {}^2D$	$34,857.8$	$39,904.5$
Titanium I $(3d)^2 (4s)^2$	$^3F - {}^1D$	$6,131.02$	$7,069.62$
	$^3F - {}^3P$	$7,099.02$	$8,324.8$
	$^3F - {}^1G$	$9,443.88$	$11,932.79$
Vanadium IV $(3d)^2$	$^3F - {}^1D$	$7,810.79$	$10,611.0$
	$^3F - {}^3P$	$9,044.00$	$12.930.4$
	$^3F - {}^1G$	$12,031.3$	$18,040.0$
Chromium V $(3d)^2$	$^3F - {}^1D$	$9,490.51$	$12,647.0$
	$^3F - {}^3P$	$10,988.9$	$15,190.0$
	$^3F - {}^1G$	$14,618.7$	$21,510.0$
Manganese VI $(3d)^2$	$^3F - {}^1D$	$11,170.3$	$14,531.$
	$^3F - {}^3P$	$12,933.9$	$17,350.7$
	$^3F - {}^1G$	$17,206.1$	$24,706.$
Iron VII $(3d)^2$	$^3F - {}^1D$	$12,850.0$	$16,350.$
	$^3F - {}^3P$	$14,878.8$	$19,455.$
	$^3F - {}^1G$	$19,793.5$	$27,790.$
Vanadium I $(3d)^3 (4s)^2$	$^4F - {}^4P$	$8,363.25$	$9,415.24$

Table 17-1 (con'd)

	Multiplet Separation	Calculated Separation	Observed Separation
Chromium IV $(3d)^3$	$^4F - {}^4P$	$10,308.2$ cm^{-1}	$13,816.$ cm^{-1}
Manganese V $(3d)^3$	$^4F - {}^4P$	$12,253.2$	$16,004.$
Iron VI $(3d)^3$	$^4F - {}^4P$	$14,198.1$	$18,169.$
Cobalt VII $(3d)^3$	$^4F - {}^4P$	$16,143.1$	$20,271.$
Cobalt I $(3d)^7(4s)^2$	$^4F - {}^4P$	$13,420.1$	$13,068.98$
Nickel I $(3d)^8(4s)^2$	$^3F - {}^3P$	$14,684.4$	$14,604.17$

The "observed separations" were obtained in all cases by averaging the fine structure splittings in the levels concerned. The experimental data were taken from Atomic Energy Levels, Charlotte E. Moore, Circular of the National Bureau of Standards 467, 1949.

By definition, $r(a)$ is the smaller, $r(b)$ the larger of r and r'. The G^k integral is expressed as a similar sum. A table of L functions was made for n_i, n_j and k values from zero to four, which is adequate to evaluate integrals involving electrons up to the 3d shell.

The ground state multiplet separations have been worked out for a number of elements. These results are given in Table 17-1. The multiplet separations for the $(3d)^2$ configurations reduce to linear functions of atomic number and are given by:

$$^3F - {}^3P = 5,834.8 \, Z_4$$

$$^3F - {}^1G = 7,762.1 \, Z_4$$

$$^3F - {}^1D = 5,039.2 \, Z_4 \qquad Z_4 \equiv \frac{Z - S}{3}$$

$$^3F - {}^1S = 19,387. \, Z_4$$

There is good agreement between the slopes of the observed and theoretical separations as a function of Z. The $(3d)^3$, ^4F - ^4P separation exhibits the same linearity in atomic number. The apparent accuracy in calculating the $(3d)^7$ and $(3d)^8$ multiplet separations is somewhat accidental.

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J. R. Schrieffer

18. AN ANALYTIC DETERMINATION OF ATOMIC ENERGY LEVELS IN MAGNESIUM

Atomic energy levels for magnesium in various states of ionization and excitation were calculated using the determinantal method.[1] The experimental and calculated values for the configurations; $1s^2$, $1s^2 2s^2 2p^6$, $1s^2 2s^2 2p^6 3s^2$, $1s^2 2s^2 2p^6 3s 3p$ (^3P and ^1P) are given in Table 18-1. For the closed shell configurations a single determinant was used. For the 3s3p energy level a secular equation corresponding to the spin-orbital degeneracy was solved.

Table 18-1

Configuration	Experimental value (cm^{-1})	Calculated value (cm^{-1})	Error percentage
$1s^2$	-3.0011×10^7	-2.9963×10^7	.15
$1s^2 2s^2 2p^6$	-4.3759×10^7	-4.3437×10^7	.74
$1s^2 2s^2 2p^6 3s 3p$			
^3P	-4.3931×10^7	-4.3589×10^7	.78
^1P	-4.3944×10^7	-4.3614×10^7	.78

The one-electron wave functions used in the determinants were an orthonormal set formed from linear combinations of simple analytic shielding constant wave functions.[2] The normalized radial wave functions used are given in Table 18-2.

Table 18-2

n	l	R_{nl}
1	0	$80.0403\, e^{-11.7r}$
2	0	$23.7035\, e^{-11.7r} - 36.7556\, e^{-3.925r}$
2	1	$35.2426\, r\, e^{-3.925r}$
3	0	$2.57834\, e^{-11.7r} - 4.25902\, r\, e^{-3.925r} + .354533\, r^2 e^{-.95r}$
3	1	$3.93672\, r\, e^{-3.925r} - .354539\, r^2 e^{-.95r}$

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A. C. Switendick

19. THERMAL VIBRATIONS OF CU-ZN SYSTEM CRYSTALS

The determination of the various branches of the normal vibration frequency versus reciprocal lattice vector contour map and the associated frequency spectra (number of normal frequency modes per unit frequency range) of the nuclear framework of crystals is of direct interest in the thermal diffuse scattering of x-rays, in restrahlen and Raman spectra interpretation, and in the calculation of such thermodynamic quantities as specific heats and coefficients of thermal expansion. There are three main aspects of the problem as treated on the Born-von Karman model: (1) the determination of the generalized force constants between nuclei ("dynamical matrix" elements of Born[1]), which appear in the Taylor expansion of the nuclear potential energy (about the equilibrium cohesive energy value at which all first derivative or force terms are zero) as coefficients of the terms quadratic in the displacements of the nuclei from equilibrium; (2) the transformation of the coupled equations of motion of the nuclei into the normal coordinate form of linear, homogeneous, algebraic equations in the amplitudes of the normal coordinates; (3) the solution for the normal frequencies of the resulting consistency determinants of order three times the number of atoms per unit cell, and the calculation of the frequency spectrum either from this frequency plot or directly from these secular determinants.

Inherent in the method in the standard form, of course, is a neglect of quartic and higher order displacement terms in the potential energy, which would lead to anharmonic effects.[2] Step (2) above is equivalent to the well-known problem of diagonalization of quadratic forms[3] (here the simultaneous diagonalization of the kinetic energy quadratic terms in the velocities and the potential energy quadratic terms in the coordinates), and if the unit cell is simple this step presents little formal difficulty. Much attention has been focused on step (3), in which the sampling procedure of Blackman,[4] the moment method of Montroll,[5] and various graphical and mechanical methods for obtaining the frequency spectrum have all been used. The recent work of von Hove[6] on the topology of the frequency contour map has provided a basic understanding of the general features of the frequency spectrum. Quite often step (1) is not handled with as much care as the other two. Where real crystals are treated the force constants are usually determined from experimental values of the elastic constants. In order to reduce the number of independent parameters to the number of independent elastic constants and for general simplification, a number of assumptions are often made; namely, those of crystal isotropy; central forces; the potential being a sum of interaction energy terms between atoms taken only two at a time; and the vanishing of force constants for neighbors further away than second or third nearest (save for ionic crystals[7]).[8]

In the present treatment of Cu-Zn system crystals particular attention is being paid to the problem of determining the force constants in as general and rigorous a way as possible. The symmetry properties of the crystals, as formulated in terms

of the well-known theory of the representations of space groups,[9] are of great help in simplifying this problem.[10] In obtaining the remaining independent force constants considerable use is to be made of the experimental results being obtained on the frequency contour maps of these crystals in the work of the x-ray group of Professor B. E. Warren at M. I. T. cn the temperature diffuse scattering of x-rays.[1, 11]

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H. C. White